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# Validation Data for Photochemical Mechanisms

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This report describes the Quality Assurance and data processing procedures and systems used at the UNC outdoor smog chamber facility. This facility is used to measure the reactants and products that participate in the photochemical smog formation process. The intent of the Quality Assurance effort is to insure the collection, transfer, processing and reporting of accurate, high resolution data without loss or distortion. This document describes the calibration techniques and data processing procedures and the processing of the experimental data. A description and examples of the format of the final documentation and data file are given. Also included are the Quality Assurance steps and accuracy and precision aspects of the data.

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# Abstract

This report describes the Quality Assurance and Data Processing procedures and systems used at the UNC Outdoor Smog Chamber Facility. The primary product of research conducted at this facility is information in the form of measurements of reactants and products in photochemical systems and measurements of the critical parameters that influence the chemical transformations system.

Generating useful data begins with understanding the goals of the project and the special needs and concerns of conducting a successful smog chamber operation. The system components are designed to collect, transfer, process, and report accurate, high resolution data without loss or distortion. The system components in the Quality Assurance and Data Processing system are: people, hardware, software, checklists, and data bases.

Quality assurance checks are made at every level of the program. Pressurized gas tank and liquid mixtures were used to establish experimental conditions of HC assuring consistency throughout the program. Several NBS traceable standards and liquid injections into the chamber used for calibration have been intercompared and show good agreement. Resulting calibration data indicates good instrument stability during the program.

The document describes the calibration techniques and data processing procedures, and the processing of experimental data. A description and examples of the format of the final documentation and data file are given. The last chapter summarizes the Quality Assurance steps and important accuracy and precision aspects of the data quality.

# Contents

1 Overall QA Steps 1

Introduction 1

Clearly Established Goals 1

Facilities and Analytical Support Requirements 2

Planning of Activities 2
  Calibrations 2
  Characterization Runs 2
  Special Mixtures 2
  Special Techniques 4

Reviewing and Scheduling Methods 4
  Priority of Runs 4
  Use of NOAA Weather Radio 4
  Feedback Scheduling 5

Site Operation 5
  Lab Air Conditioner 5
  Smog Chamber 5
  Chamber Sampling Manifold 6
  Chamber AC Drying System 6
  Ethylene Convertor 6
  Mass Balance 6
  Supplies 6

Check Lists 7
  Setup Checkout Lists 7
  Operator Checkout List 7
  Run Checkout List 7
  Run Packup List 7

Preventative Maintenance 7

Characterization Experiments 8
  Types of Characterization Experiments 8
  Frequency 9

2 System Components 10

Location of Work 10
  Experimental Site 10
  Data Processing Location 10

Personnel 10
  Advisory Group, AG 11
  Administrative Research Assistant, AA 11
  Project Coordinator, PC 11
  Site Operator, SO 11
  Peak Picker, PP 11
  Computer Technician, CT 11

Computers Used 11
  DEC PDP-11/40 11
  DEC LSI-11/23 12
  IBM PC 12
  DEC VAX-11/780 12

Computer Programs Used 13
  Description of General Purpose Programs 13
  Description of Specific Programs 13

Description of Data File Formats and Contents 14
  "U" file 14
  "G" file 14
  "P" files 15
  "C" files 15
  "K" files 16
  "R" files 16
  "Q" files 16
  "A" files 16
  "E" files 16
  ACDTR.COM file 16

Description of Databases 16

Description of Database Procedures 17
  List of all DTR Procedures by Name and Function 17
  Worksheets/Databases 18

3 Calibration 20

Approach 20

**NBS-Traceable Sources** . . . . . . . . . . . . . . . . . . . . . . . . . 20
- NO and O3 Sources . . . . . . . . . . . . . . . . . . . . . . . 20
- Hydrocarbon Sources . . . . . . . . . . . . . . . . . . . . . . 21
- Transfer Standards Created from Primary Sources . . . . . . . . . 22

**Primary Source Comparison** . . . . . . . . . . . . . . . . . . . . . 22
- NO and O3 Sources . . . . . . . . . . . . . . . . . . . . . . . 22
- Hydrocarbon Sources . . . . . . . . . . . . . . . . . . . . . . 28

**Transfer Calibration to working "AUTOCAL" Sources** . . . . . . . . . . 28
- NOx and O3 Calibration Sources . . . . . . . . . . . . . . . . . 28
- Manual Gas Phase Titration . . . . . . . . . . . . . . . . . . . 28
- Hydrocarbon Sources . . . . . . . . . . . . . . . . . . . . . . 32

**Routine NOx and O3 Calibrations Methods** . . . . . . . . . . . . . . 45
- Automatic Source Sampling . . . . . . . . . . . . . . . . . . . 45

**Routine HC Calibrations** . . . . . . . . . . . . . . . . . . . . . . 45
- Automatic Source Sampling . . . . . . . . . . . . . . . . . . . 46
- Manual Precision Liquid Injections . . . . . . . . . . . . . . . 46

**Meteorological Sensor Calibrations** . . . . . . . . . . . . . . . . . 47
- Solar/UV radiation Calibrations . . . . . . . . . . . . . . . . 47
- Temperature Calibrations . . . . . . . . . . . . . . . . . . . . 47
- Dewpoint Calibrations . . . . . . . . . . . . . . . . . . . . . 47

**Flowrate Measurements - Calibration** . . . . . . . . . . . . . . . . 48

**Time Measurement - Clock Calibration** . . . . . . . . . . . . . . . . 48

**Calibration Documentation and Processing Databases** . . . . . . . . . 48
- Paper Forms . . . . . . . . . . . . . . . . . . . . . . . . . . 48
- Electronic Forms and Other Documentation . . . . . . . . . . . . 49
- Calibration Data Processing Status Database (CALENTRY . . . . . . 53
- Calibration Databases . . . . . . . . . . . . . . . . . . . . . 53
- Security of Calibration Databases . . . . . . . . . . . . . . . 57

**Calibration Data Processing** . . . . . . . . . . . . . . . . . . . . 58
- $NO_x$ and $O_3$ . . . . . . . . . . . . . . . . . . . . . . . . 58
- HC Processing . . . . . . . . . . . . . . . . . . . . . . . . . 59

**4 Experimental Data** 78

**Experimental Results Documentation** . . . . . . . . . . . . . . . . . . . 78
  Data . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 78
  Forms . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 79
  Plots . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 85
  Run Data Processing Status Databases . . . . . . . . . . . . . . . . 85

**Description of Data Processing Status Database** . . . . . . . . . . . . . 96
  Description . . . . . . . . . . . . . . . . . . . . . . . . . . . . 96
  Use of Data Processing Status Database . . . . . . . . . . . . . . . 96

**Digital Voltmeter Data Processing** . . . . . . . . . . . . . . . . . . . 98

**Strip Chart Data Processing** . . . . . . . . . . . . . . . . . . . . . . 102

**Documentation Processing** . . . . . . . . . . . . . . . . . . . . . . . 106
  General Documentation Form . . . . . . . . . . . . . . . . . . . . . 107
  General Description and Purpose of Experiment . . . . . . . . . . . . 107
  Initial Conditions . . . . . . . . . . . . . . . . . . . . . . . . . 107
  Meteorological Conditions . . . . . . . . . . . . . . . . . . . . . . 109
  Data Times, Data Exceptions, Special Problems and Concerns . . . . . . 109
  Quality Assessment . . . . . . . . . . . . . . . . . . . . . . . . . 109
  Documentation File Production . . . . . . . . . . . . . . . . . . . . 112

**Final Segmented File Production** . . . . . . . . . . . . . . . . . . . . 112

**Security of Data** . . . . . . . . . . . . . . . . . . . . . . . . . . . 114
  Inventory . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 114
  Retention of Data . . . . . . . . . . . . . . . . . . . . . . . . . 114
  Backup of Data . . . . . . . . . . . . . . . . . . . . . . . . . . . 114

**5 Segmented Data File** 115

**General Description** . . . . . . . . . . . . . . . . . . . . . . . . . . 115

**File Formats** . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 116

**ANSI Tape File Format** . . . . . . . . . . . . . . . . . . . . . . . . . 116

**Tape Contents** . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 120

**Final Data Plots made from SegFile** . . . . . . . . . . . . . . . . . . . 120

6 Summary of QA 131

Summary of Calibration and Data QA . . . . . . . . . . . . . . . . . . 131

List of QA Steps . . . . . . . . . . . . . . . . . . . . . . . . . . . 132
- Before Runs . . . . . . . . . . . . . . . . . . . . . . . . . . . 132
- After Run-Experiment Logging . . . . . . . . . . . . . . . . . . 132
- During Calibration . . . . . . . . . . . . . . . . . . . . . . . 133
- During DVM Data Processing . . . . . . . . . . . . . . . . . . . 134
- During GC Data Processing . . . . . . . . . . . . . . . . . . . 135
- During Documentation Stages . . . . . . . . . . . . . . . . . . 136
- After SegFile Made . . . . . . . . . . . . . . . . . . . . . . . 137

A Site Checklists 140

Checklist For 0900 EDT Site Operator. . . . . . . . . . . . . . . . . 140
- Outside Check . . . . . . . . . . . . . . . . . . . . . . . . . . 140
- TSR and UV zero check . . . . . . . . . . . . . . . . . . . . . 143
- GC Check . . . . . . . . . . . . . . . . . . . . . . . . . . . . 143

Checklist for Leaving the Site Set Up for a Run . . . . . . . . . . . 145
- Computer . . . . . . . . . . . . . . . . . . . . . . . . . . . . 145
- Formaldehyde . . . . . . . . . . . . . . . . . . . . . . . . . . 145
- NOx and O3 Instruments . . . . . . . . . . . . . . . . . . . . . 145
- TSR and UV Chart . . . . . . . . . . . . . . . . . . . . . . . . 146
- Charts . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 146
- Carle I . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 147
- Carle II and Carle III . . . . . . . . . . . . . . . . . . . . . 147
- Sigma 10 Integrator . . . . . . . . . . . . . . . . . . . . . . 148
- Dew Point Meter . . . . . . . . . . . . . . . . . . . . . . . . 149
- ATC and Varian . . . . . . . . . . . . . . . . . . . . . . . . . 149
- CO Meter . . . . . . . . . . . . . . . . . . . . . . . . . . . . 149
- Air Generators . . . . . . . . . . . . . . . . . . . . . . . . . 149
- General . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 150

Early Morning Checkout . . . . . . . . . . . . . . . . . . . . . . . . 152

Run Pack-Up Checklist . . . . . . . . . . . . . . . . . . . . . . . . 154

B HC Cal Sources Certification 155

C Official Calibration Sources 177

D CALANA Plots and Reports 186

E Solar/UV Radiation 227

General Description Of Light Radiometers . . . . . . . . . . . . . . . . . . 227

General Description Of Light Measurement . . . . . . . . . . . . . . . . . 227

General Operating Procedure . . . . . . . . . . . . . . . . . . . . . . . 230

Radiometer And Calibration History . . . . . . . . . . . . . . . . . . . . 230

Calibration Procedures . . . . . . . . . . . . . . . . . . . . . . . . . . 230

Uncertainty In Light Data . . . . . . . . . . . . . . . . . . . . . . . . 233
  Absolute Light Measurements . . . . . . . . . . . . . . . . . . . . . 234
  Time and Solar Events . . . . . . . . . . . . . . . . . . . . . . . . 235

Albedo And Local Topography . . . . . . . . . . . . . . . . . . . . . . 243

Position Of Radiometers . . . . . . . . . . . . . . . . . . . . . . . . 243

Sun Path, Trees And Chamber Structure Shading . . . . . . . . . . . . . 243

Data Acquisition . . . . . . . . . . . . . . . . . . . . . . . . . . . . 245

Correction Factors For UNC Light Data . . . . . . . . . . . . . . . . . 245

F Chamber and Facility 259

G Analytical Methods 266

# Tables

1. Target Experiments . . . . . 3
2. NO Tank Calibration Sources . . . . . 21
3. HC Tank and Liquid Calibration Sources . . . . . 21
4. OCS from Injections in Chamber . . . . . 23
5. Species ID numbers and Properties . . . . . 27
6. Comparison of Primary NO Calibration Sources . . . . . 30
7. Intercomparisons Among Sources . . . . . 43
8. Comparison of Primary HC Calibration Sources . . . . . 44
9. Processing System for Instrument Auto-Calibration Data . . . . . 54
10. CALSUM Example . . . . . 55
11. $NO_X$ and $O_3$ Calibrations for 1984 . . . . . 61
12. $NO_X$ and $O_3$ Calibrations for 1985 . . . . . 64
13. Processing System for Instrument Auto-Calibration Data . . . . . 67
14. Table 14. Summary of CALANA Statistics . . . . . 73
15. Table 14. Summary of CALANA Statistics for 1985 . . . . . 74
16. Record Description for RUNENTRY Database System. . . . . . 87
17. RUNENTRY Processing Summary for September 14, 1981 . . . . . 88
18. Processing System for DVM Data . . . . . 100
19. Processing System for Instrument Data . . . . . 104
20. Documentation Steps . . . . . 107
21. Final Segmented File Production Steps . . . . . 113
22. Example Segmented Data File . . . . . 117
23. VAX/VMS ANSI VOL1 Label . . . . . 127
24. First File Header Label (HDR1) Fields . . . . . 128
25. Second File Header Label (HDR2) Fields . . . . . 129
26. Third File Header Label (HDR3) Fields . . . . . 130

# Figures

**1.** Comparison of Primary NO Calibration Sources . . . . . 29
**2.** $NO_x$ and $O_3$ Cal Processing Flowchart . . . . . 33
**3.** LOTUS Spreadsheet for Manual Cal Processing . . . . . 34
**4.** LOTUS Analysis Spreadsheet of Manual Cal 1984 . . . . . 36
**5.** LOTUS Analysis Spreadsheet of Manual Cal 1985 . . . . . 38
**6.** LOTUS Analysis Spreadsheet Manual Cal 1984 Plots . . . . . 41
**7.** LOTUS Analysis Spreadsheet Manual Cal 1985 Plots . . . . . 42
**8.** Official Calibration Source Form . . . . . 50
**9.** Cal Pick Instruction Form . . . . . 52
**10.** AUTOCAL Processing Flowchart . . . . . 60
**11.** HC autocal processing flowchart . . . . . 66
**12.** CALANA example figures . . . . . 70
**13.** calextr examples . . . . . 76
**14.** Runsheet . . . . . 81
**15.** Instrument Checklist Form . . . . . 82
**16.** Run Folder Inventory Checksheet Form . . . . . 83
**17.** Data Processing Instruction Form . . . . . 84
**18.** Runentry Welcome and Main Menu Screens . . . . . 89
**19.** RUNENTRY Date and Display Selection Screens . . . . . 90
**20.** RUNENTRY General, Documentation, and File Status Screens . . . . . 91
**21.** RUNENTRY DVM and Picked Instrument Status Screens . . . . . 92
**22.** PC Report Example . . . . . 94
**23.** DVM Processing Flowchart (Computers and Files) . . . . . 99
**24.** Instrument Processing Flowchart (Computers and Files) . . . . . 103
**25.** Documentation Processing Flowchart (Computers and Files) . . . . . 108
**26.** Basic Layout of a VAX/VMS ANSI Labeled Volume . . . . . 121
**27.** Single File/Single Volume Configuration . . . . . 122
**28.** Multifile/Multivolume Configuration . . . . . 123
**29.** VAX/VMS ANSI VOL1 Label Format . . . . . 123
**30.** HDR1 Label Format . . . . . 124
**31.** HDR2 Label Format . . . . . 125
**32.** Blocked Fixed-Length Records . . . . . 126
**33.** Variable-Length Records . . . . . 126

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# 1

# Overall QA Steps

## Introduction

There are a number of general activities that contribute to overall quality in the experimental data. These include:

- having clearly established experimental program goals;
- establishing facilities and analytical support requirements;
- planning activities for experimental and quality assurance programs required to achieve goals;
- reviewing and scheduling activities;
- maintaining basic Research Site Facility;
- using checklists;
- using preventative maintenance;
- performing special test experiments routinely.

Each of these will be discussed further.

## Clearly Established Goals

The most basic part of a QA program is to assure that efforts are properly designed and directed towards clearly defined goals. This assures that the data obtained will satisfy the needs of the program. The approach and design of the experimental program and the selection of experiments are as important as the accuracy and precision aspects of the final data. A range of experiments conducted with appropriate chemical conditions must be identified. Minimum data requirements must be determined beforehand to assure that the results will be useful to achieve the program goals.

The experimental conditions of interest must be identified and prioritized. The number of experiments to be performed are decided based upon program goals, approach, design and resources.

Once an experimental program is designed, a table of Prioritized Target Conditions can be made to guide the experimental program. An example table is shown in Table 1.

Specific experimental conditions of species (and sources) and amounts (chamber concentrations: milligrams of solids, microliters of liquids, or seconds at specific flowrates of gases) are calculated by the project coordinator and recorded on the Run Sheet used to conduct the experiment to assure that the proper experiment is conducted. This form will be discussed further in the chapter entitled "Experimental Data Processing".

## Facilities and Analytical Support Requirements

The facilities and analytical support requirements must be identified. Special modifications or implementation of new analytical methods consume resources. These activities could potentially hinder the attainment of the project goals if problems are encountered. Facilities and analytical capabilities are described in two Appendices attached to each Final Report.

## Planning of Activities

### Calibrations

All instruments must be calibrated frequently to assure accuracy and to determine precision. Along with scheduling the experimental program, scheduling of calibrations are required to assure that the data can be processed with minimal uncertainty. Calibration procedures will be discussed in the next chapter.

### Characterization Runs

Several types of smog chamber experiments are generally conducted to characterize aspects which can effect interpretation of experimental results and aid modelers. These are performed throughout the programs. A discussion of chamber background reactivity was given in Jeffries and Sexton[1,2].

**Table 1.** Experiments To Be Performed In 1985

| BLUE SIDE | RED SIDE |
|---|---|
| All Static<br>1.8 ppmC Urban Mix<br>0.2 ppm NOx | Continuous Injection; Dilution<br>1.8 ppmC Urban Mix<br>0.2 ppm NOx |
| All Static<br>1.0 ppmC Urban Mix<br>0.2 ppm NOx | Continuous Injection; Dilution<br>1.0 ppmC Urban Mix<br>0.2 ppm NOx |
| Static Injection<br>3.00 ppmC Formaldehyde<br>0.4 ppm NOx | Static Injection<br>1.50 ppmC Formaldehyde<br>0.4 ppm NOx |
| Static Injection<br>2.40 ppmC Urban Mix<br>0.60 ppmC Formaldehyde<br>0.4 ppm NOx | Static Injection<br>2.70 ppmC Urban Mix<br>0.30 ppmC Formaldehyde<br>0.4 ppm NOx |
| Static Injection<br>2.00 ppmC Syn-Auto Mix<br>0.25 ppmC Toluene<br>0.75 ppmC m-Xylene<br>0.4 ppm NOx | Static Injection<br>2.00 ppmC Syn-Auto Mix<br>0.75 ppmC Toluene<br>0.25 ppmC m-Xylene<br>0.4 ppm NOx |
| Static Injection<br>0.50 ppmC Toluene<br>0.50 ppmC Ethylbenzene<br>0.50 ppmC m-Xylene<br>0.50 ppmC o-Xylene<br>0.50 ppmC 1,2,4-t-mth-benzene<br>0.50 ppmC 1,2,3-t-mth-benzene<br>0.4 ppm NOx | Static Injection<br>1.00 ppmC Toluene<br>0.50 ppmC Ethylbenzene<br>0.25 ppmC m-Xylene<br>0.50 ppmC o-Xylene<br>0.25 ppmC 1,2,4-t-mth-benzene<br>0.50 ppmC 1,2,3-t-mth-benzene<br>0.4 ppm NOx |

Investigate the relationship between solar radiation sensor reading and the photolysis rates in the chamber. This will include placing sensors inside the chamber and conducting an analysis of TSR/UV data in the data set.

### Special Mixtures

The experiments often utilize synthetic mixtures. These mixtures require extensive experimental support. For example, previous experiments may compare the reactivity of these mixtures with real auto exhaust or with other synthetic mixtures which are further compared with simpler photochemical systems. This previous experimental experience is an additional QA step which assures reference to well-studied photochemical systems.

These mixtures are either ordered from scientific gas suppliers or are mixed and prepared on site. In either case, the resulting mixtures are compared with NBS-traceable calibration sources.

### Special Techniques

Some project goals require the development of special techniques such as the production of a particular dilution rate profile or the use of highly labile compounds such as methyl nitrite. To use methyl nitrite requires that the synthesis, storage and use (injection into chamber) techniques be developed and implemented.

## Reviewing and Scheduling Methods

To maximize the quality of program results, reviewing and careful scheduling are needed throughout the program. Important considerations are the priority of the experiments, status of the smog chamber site facilities, weather, and previous experimental results. Inherent in this process is a continuous review of experimental results to assure that target conditions are being attained and experimental conditions were satisfactory.

### Priority of Runs

The results of experiments are affected by the initial concentration conditions, even for the same composition of ozone precursors. For most studies, several experiments are desired. Higher priorities are assigned to those experiments which will yield the most information for the more average conditions. Later experiments are used to establish the range of conditions or to establish more basic results to assist in interpretation.

### Use of NOAA Weather Radio

Outdoor Smog Chambers are subjected to real weather situations. This leads to difficulties in scheduling runs. To provide up-to-the-minute information needed to schedule runs, we use a weather radio to receive the airport NOAA weather radio station. Weather reports are updated every hour and forecasts are made every 3 minutes. The most desirable conditions are clear, sunny, dry and warm.

When clear weather is forecast, the site operator is contacted by telephone. He gives a status report of the site facilities and instrumentation. The next highest priority experiment which can be conducted considering the current status of the facilities is then scheduled.

When cloudy weather is forecast ("partly cloudy") with a low probability of rain, a characterization experiment is scheduled unless a set of calibrations are needed and the long range forecast is for good weather.

When rainy or "mostly cloudy" weather is forecast, a "CAL DAY" is scheduled.

### Feedback Scheduling

Experimental results are reviewed frequently. Experiments are repeated or new experiments are designed and scheduled depending on the conditions or outcome of experiments already conducted.

## Site Operation

A great deal of QA occurs in the routine operation of the smog chamber site. Procedures more basic than calibrations are required to assure useful and complete data. The laboratory itself must be maintained. Adequate supplies must be in place, all documentation must be complete, instruments must be in good operating order, support equipment must be checked-out, and the chamber must be cleaned and leak-checked.

### Lab Air Conditioner

The laboratory air conditioner maintains a consistent environment needed for the operation of instruments and computers in the typical 95°F, high humidity, summer conditions in North Carolina. Lab temperature is monitored continuously by the computer data acquisition system and is reported in the final distributed experimental results segmented data file. The lab temperature is maintained at 75°F. The air conditioner is checked at the beginning of every run season by a professional service. The filter is changed every three weeks during most of the season and every two weeks during the warmest part of the season.

## Smog Chamber

The smog chamber itself requires routine maintenance. It is frequently checked for holes and leaks, which are repaired. Occasionally insects find their way into the chambers and must be removed. The floor is swept and sponged with distilled water when needed. The automated venting doors and air drying ductwork is checked daily. Leaks are often discovered by analysis (least-squares exponential fit: see section on computer programs below) of the inert tracer data collected during every run on both sides of the dual chamber.

## Chamber Sampling Manifold

The sampling manifold is routinely checked for breaks. It is warmed with electric heat tapes the entire length from the chamber to the fans inside the laboratory. Minor leaks can be discovered by analysis of the inert tracer data collected during every run on both sides of the dual chamber. The manifold is checked daily for breaks, inoperating heating lines by touch, and by appearance of condensation (warm chamber air into a cooler laboratory).

## Chamber AC Drying System

An automated chamber air drying system in place under the chamber is used before experiments to prevent condensation which might form during the cool morning hours after venting the chambers. A Freon check and general maintenance checkout is performed at the beginning of every run season. Testing is performed early in the season to measure the dewpoint depression capability. Routine monitoring of daily performance (for each experiment) is the most common QA procedure. Dewpoint is continuously monitored. Condensation is checked by the morning operator.

## Ethylene Convertor

The ozone monitor utilizes ethylene. The excess is routed through a heated convertor which oxidizes it. Untreated excess ethylene can be a severe contamination problem. To check for leaks in the ethylene treatment system, two GC-FID systems (Carles 1 and 2) monitor for this possible contamination in background chamber air analyses before every experiment.

## Mass Balance

A high precision Mettler balance is used for weighing chemicals used for reagents and paraformaldehyde used for injection of formaldehyde into the chamber.

### Supplies

An inventory is performed at the beginning of every run season to determine supplies which must be ordered long in advance of the run season. Special mixtures of HC and other precursors must also be ordered. More common supplies are tracked and stocked routinely. During the run season, the use of expendable supplies is carefully monitored and reordered when necessary.

## Check Lists

Many details must be checked to assure that a smog chamber experiment will be successful. Several checklists are used before, during, and after experiments.

### Setup Checkout Lists

To make sure that things are ready for an experiment the next day, a setup checkout list is used. All supplies (gases, *etc.*), computer and instrument switch settings, and injection gases are checked; syringes and liquid chemicals are set out; the run sheet is filled out; venting is checked; the manifold is checked for leaks, *etc*. This checklist is shown in Appendix A.

### Operator Checkout List

For the early morning operator responsible for initiating the experiment, another checklist is used. This is somewhat redundant to the setup list to check extremely important details that might have been overlooked by the setup operator. In addition, check items include details about proper operation of instruments, manifold, and chamber, injections of chemical precursors, and recording documentation about details of experiment. This list is also shown in Appendix A.

### Run Checkout List

Another checkout list is used by site personnel that arrive at mid-morning. Check items include checking on status of instruments, stripchart recorders, computer, chamber, *etc.* to assure successful continuation of the experiment and data acquisition. This list is also given in Appendix A.

### Run Packup List

This list is primarily an inventory checklist to insure that all data is properly packed up, documented, and returned to the School of Public Health data processing office. This list is included in Appendix A.

## Preventative Maintenance

To assure proper operation of all instruments, the smog chamber, support facilities, instrument stability (reflected in "cal factor variation"), and maximum "up-time," preventative maintenance is routinely performed.

## Characterization Experiments

As mentioned above, characterization experiments are performed routinely. These experiments are used by modelers to determine the importance of chamber artifact processes. Background, reactivity, surface processes (such as off-gasing of $NO_x$, HCHO), decay of $O_3$ and $NO_x$ are of primary interest. Previous experiments conducted over several years have been studied to characterize these and other aspects of chamber behavior. Benchmark experiments are also routinely performed. These include propylene and $NO_x$ experiments.

### Types of Characterization Experiments

*Background*

This experiment shows how much $O_3$ is formed when no chemical precursors are injected into the chamber except for the rural air used in venting and any material which may remain on the chamber walls after venting.

*O3 Decay*

$O_3$ is injected into otherwise clean air and allowed to decay. The rate is determined. This experiment is usually performed at night. Some modelers include this decay process although the rate is very low.

*NO Oxidation, Daytime*

NO is injected into clean chamber air (nothing else injected) to detect sources of radicals. The rate of oxidation is observed. The magnitude of and types of chamber radical sources required to achieve the observed rate can be estimated by modeling. To modify the test, CO can be added to one side to help determine the type of radical source. The CO changes the balance of $HO^\cdot$ and $HO_2^\cdot$ radicals without adding any radicals to the system itself.

*NO Decay, Nighttime*

This experiment is conducted like the one described above except that no sunlight is involved.

### *Acetaldehyde and CO*

Matched injections of acetaldehyde (usually 1 ppmC) are made into each chamber. One side has CO injected (usually 50 ppm). This experiment forms PAN which can aid in detecting any wall $NO_x$ off-gasses. The CO changes the balance of $HO^\cdot$ and $HO_2^\cdot$ radicals without adding any radicals to the system itself.

### *Formaldehyde and CO*

Matched injections of formaldehyde are made into each chamber. One side has CO injected (usually 50 ppm). Formaldehyde photolyzes to produce $HO_2^\cdot$ and CO. Without injected $NO_x$, only the background $NO_x$ in the rural air or from the chamber walls can participate in this system. Any $HO^\cdot$ produced can react with formaldehyde or with the additional CO added to one side. The CO changes the balance of $HO^\cdot$ and $HO_2^\cdot$ radicals without adding any radicals to the system itself.

### *Propylene and NOx*

Matched conditions of propylene and $NO_x$ have been used for years as a benchmarking experiment. Experience has shown that experiments conducted on the same day a year apart can be duplicated if the sunlight quality is good. Demonstrating matched results from the two chambers is another reason for conducting matched condition experiments.

## Frequency

These experiments should be conducted routinely. However, they are not conducted as frequently when the program falls behind schedule because of poor weather. These experiments have been studied and the range of magnitude of these chamber processes is well known.

# 2

# System Components

This section lists and describes the system components. Major types of tasks and responsibilities have been organized and assigned to different people. Computers, instruments and other hardware are used to generate and process data. Many computer programs (software) are used. Policies and procedures have been developed to assure proper and consistent treatment of the data. Databases have been created to organize and to aid in retrieving and processing the large amounts of calibration data.

## Location of Work

The research work occurs in two different locations. The experiments are conducted at the Smog Chamber Site located in a rural area with relatively clean background air, and the data is processed on the University campus.

### Experimental Site

The site is located in Chatham County, North Carolina, approximately 30 kilometers from the University of North Carolina at Chapel Hill, and approximately 8 kilometers from the small town of Pittsboro. Chatham County is one of the most rural, least industralized counties in North Carolina and is heavily wooded. The background concentrations of $NO_x$ and NMHC are usually less than 5 ppbC and less than 80 ppbC, respectively. More importantly, the air exhibits very low reactivity in the chamber.

### Data Processing Location

The data are processed in the School of Public Health on the campus of UNC, where all computers and data processing facilities are easily accessible.

## Personnel

A number of people with different tasks contribute to the process of conducting smog chamber experiments and processing the results. The names and roles of these people are listed below.

### Advisory Group, AG

An advisory group, consisting of the principal investigator, the co-principal investigator, the project coordinator, and the administrative research assistant meet frequently to review the progress of each project.

### Administrative Research Assistant, AA

The administrative research assistant is responsible for logging the experiments and calibrations, ordering supplies, and managing the budget.

### Project Coordinator, PC

The project coordinator oversees the experimental program and the processing of the data.

### Site Operator, SO

Site operators are responsible for maintenance, calibration, and operation of the research site. They work closely with the PC to determine which experiments should be conducted next or if time should be scheduled for calibration or maintenance.

### Peak Picker, PP

The "peak pickers" process most of the data under the guidance of the PC.

### Computer Technician, CT

The computer technicians are responsible for unpacking the data from the smog chamber data acquisition system and for making tapes of segmented data files and a backup of all data processing files.

## Computers Used

Several computers are used in the program. They help conduct experiments, process data, plot data, analyze results, and aid in writing.

## DEC PDP-11/40

The DEC PDP-11/40 is used to control the experiments and perform the data acquisition for much of the data. This computer writes data to 8 inch flexible diskettes for transfer to the data processing office.

## DEC LSI-11/23

Two DEC LSI-11/23 computers are used to process most of the experimental and calibration data. Most programs are written in PASCAL. A major component is the DIGITIZER which permits rapid and accurate conversion of stripchart data to computer data files. Each computer has at least one 8 inch floppy drive and a 10 Mb hard disk. These computers can communicate to the IBM PC and to the DEC VAX-11/780.

## IBM PC

The IBM PC is used with LOTUS 123 to implement many spreadsheets and databases discussed throughout this report. It is also used for word processing. Some PASCAL programs are also used. The IBM PC uses 5 1/4 inch floppies and can "upload" and "download" data from the DEC VAX-11/780.

## DEC VAX-11/780

A DEC VAX-11/780 mainframe computer is used to maintain several large databases discussed in this report. The VAX system also makes plots and prints reports using a large, high resolution laser printer. Modeling input decks are set up and submitted from the VAX to be run on the university's IBM 4381 mainframe computer. "Printouts" and "punched" output are returned to the VAX as standard ASCII files. The VAX can also read and write to 8 inch floppies and industry standard magnetic tape.

# Computer Programs Used

## Description of General Purpose Programs

### *LOTUS 123*

LOTUS 123 is an electronic spreadsheet, database, and graphic program that runs on the IBM PC. The spreadsheet in 123 has 256 columns and 2096 rows; each column can be a different width and each cell can hold a text label, a numerical value, or a formula that includes references to other cells. When new data is entered into cells, the program automatically updates the values of all the formulas. Ranges of cells can be selected to be graphed. Graphs include line, bar, and pie; up to 6 lines can be plotted on a graph. In addition, the spreadsheet contents can be treated like a database table in which the rows are records and the columns are fields in the record. Records can be selected, deleted, copied, and sorted to an output location on the spreadsheet. The whole spreadsheet or selected parts of the spreadsheet can be printed to a printer or file. Data can also be 'imported' from other programs or files.

### *DATATRIEVE*

DATATRIEVE is a data base query, update, and report writing system running on the VAX-11. DATATRIEVE is used to maintain calibration and data processing status databases and serves a tool to coordinate effort among the PC, PP, and CT. In DATATRIEVE, the PC can ask the system to print a list of all runs that had all instrument data "picked" but did not have calibration factors determined for those instruments. From this list, the PC determines which calibration factors must be produced to complete the processing of the runs. Typical run tracking data bases grow to be 500,000 characters during a run processing season. The total size of data managed by DATATRIEVE is more than 20 million characters.

## Description of Specific Programs

*UNPACK* converts packed binary DVM data from the chamber site's DA system to ASCII format ("U files").

*FASTDV* produces temporary ("P" file) files of raw DVM data for making plots for preliminary QA procedures, and strips $NO_x$ and $O_3$ calibration data from DVM data file.

*DIGPIK* allows the digitizer to be used to convert experimental peak height data for all species for a given instrument and writes data to ("P" file) files on LSI11/23.

It also is used to digitize calibration data and produce calibration response ("R") files.

*PLOPIC* plots raw ("P" file) experimental data from both DVM or stripcharts.

*ACALAV* automatically produces average $NO_x$ and $O_3$ instrument calibration data for zeros and spans stripped from the DVM data with FASTDV.

*CALFAC* calculates calibration factors from digitized calibration data and the official calibration source file.

*CALLOK* lists and plots calibration data for a given instrument and species combination.

*CALANA* performs statistical analysis on calibration data for any combination of instrument and species.

*DVMFIX* applies calibration factors to DVM ("U" file) data and outputs concentration and physical measurement ("G") files.

*CALCON* applies calibration factors to digitized ("P" file) data from stripcharts and outputs concentration ("C" files).

*PLOCON* plots concentration ("C" file) experimental data from stripcharts.

*HCANAL* reads time/concentration data files of HC data and computes composition analysis.

*CSTAR* reads tracer data files and computes chamber dilution rate by fitting with exponential least-squares method.

## Description of Data File Formats and Contents

### "U" file

The primary data file originating from the Data Acquisition system is "U"npacked after transport from the chamber site to the data processing office. This file contains "raw" data from the $NO_x$ and $O_3$ monitors, chamber, ambient and laboratory temperature, total solar and ultraviolet light, and dewpoint monitors. The data is taken every minute alternating between the two sides. Calibration data from automatic calibrations of the $NO_x$ and $O_3$ monitors is also contained in this file.

## "G" file

The final data file processed from the primary "U" file is referred to as the "G"as Chamber file. This file contains corrected (adjusted with calibration factors) data. The final data is for four minute intervals alternating between the two sides.

The file is comprised of two parts: documentation and data. The documentation identifies the experiment. Next information pertaining to the processing of the data is given:

- source of calibration factors;
- data last processed;
- explanation of data identifiers (labels);
- explanation of units;
- explanation of data alteration.

Finally the actual calibration factors are listed. Calibration factors are specified for the beginning and ending of periods of valid data.

The data are preceded by a "header" card identifying the columns of data. Data are listed in the same order as the header card. An example of this type of file is shown in Chapter 6.

## "P" files

The data files of "P"icked data from other individual instruments which are not connected to the Data Acquisition System are produced and processed separately with more manual effort (*e.g.*measuring peak heights from gas chromatographs). This file is comprised of two parts: documentation and data. The documentation indicates:

- the source of the data;
- the data processor ("peakpicker");
- attenuation;
- units;
- species identification.

The data follows with one data point per line: the format allows for easy editing and correction during processing.

## "C" files

These are the files of final corrected "C"oncentration data processed from the "P" files. The format of these files are identical to the data portion of the "G" files. An example of this type of file is shown in Chapter 6.

## "K" files

For every "C" file there is a matching "K" file containing documentation pertaining to the source and processing of the data. In addition to the documentation originally in the "P" file is the maximum amplitude and concentration of each species in the file and the calibration factor (and source) used in processing the data. An example of this type of file is shown in Chapter 6.

## "R" files

Calibration "R"esponse data to official calibration sources other than from the $NO_x$ and $O_3$ monitors are stored in these files, which are produced from the same program which produces the "P" files (DIGPIK). They have very similar format and documentation but also include the OCS identification number.

## "Q" files

The resulting calibration factors from comparing the "R" files to the Official Calibration Sources are stored in the "Q" files along with all associated documentation from the "R" file. This file also contains DATATRIEVE commands which will store the data in the calibration DATATRIEVE database HCCAL.

## "A" files

Calibration response data from the "A"utomatic calibrations of the $NO_x$ and $O_3$ monitors are produced with FASTDV from the data stored in the "U" file.

## "E" files

The "A" files often contain data which represent a transition reading between the chamber air and the calibration source. This unwanted data is "E"dited from the file.

## ACDTR.COM file

The "E" files are processed (averaged) to a single value with a program called ACALAV which is output to a file called ACDTR.COM which also contains DATATRIEVE commands to store the data in the DATATRIEVE database AUTOCAL.

## Description of Databases

Several databases are used in processing the data and calibration data. The following are created with DATATRIEVE on the VAX-11/780. These are described in more detail in Chapter 3.

*RUNENTRY* is the primary database identifying the experiment and tracking the processing of the data from each instrument used.

*CAL_ENTRY* is the database for tracking the calibration data processing.

*CAL_SOURCES* is the database of the "O"fficial "C"alibration "S"ources OCS) including all supporting information and corresponding identification number.

*HC_CAL* is the database of the final processed calibration factors resulting from calibrations performed on the analytical instruments producing data which is not collected from the Data Acquisition System.

*AUTO_CAL* is the database of the calibration data from "auto"matically performed calibrations of the $NO_x$ and $O_3$ monitors.

*RUN_CAL_USED* is the database of the calibration factors actually used in processing the manually processed ("P" file) data.

*SPECIES* is the database of official species names and corresponding identication numbers used in data processing to assure consistency and proper spelling and identification.

## Description of Database Procedures

### List of all DTR Procedures by Name and Function

Various procedures are used with the DATATRIEVE databases to assist in accessing and using the data and producing reports or files to be used by other data processing computer programs.

*PPREPORTS* is a VAX command procedure which creates a task report for Peak Pickers (data processors running DIGPIK using DATATRIEVE and the RUNENTRY data base. The report lists each data processing step presently needing PP action, such as instrument stripcharts needing to be digitized and plotted.

*PCREPORTS* is a VAX command procedure which creates a task report for Project Coordinators using DATATRIEVE and the RUNENTRY data base. The report lists each data processing step presently needing PC action, such as various QA steps.

*CTREPORTS* is a VAX command procedure which creates a task report for Computer Technicians using DATATRIEVE and the RUNENTRY data base. The report lists each data processing step presently needing CT action, such as moving data to the VAX or vice versa.

*PRINT_SPECIES* prints a list of the official species names and corresponding identification number.

*PRINT_CAL_SOURCES* prints a list of the Official Calibration Sources including name, serial number, source date, validation date and personnel, manufacturers and the validated concentrations.

*PRINT_OCS_FILE_FOR_LSI* produces a file of the official calibration sources to be used by another program (CALFAC) used to calculate calibration factors from the calibration response data.

*PRINT_CALS_AND_FACTORS* calculates and produces a report of the calibration factors calculated from the automatic calibration data from the $NO_x$ and $O_3$ monitors from the AUTO_CAL database.

*PRINT_HC_CAL_FACTORS* produces a report of the calibration data for all the other instruments other than $NO_x$ and $O_3$monitors from the HC_CAL database.

*PRINT_RUN_CAL_USED* - produces a report of the calibration factors used by instrument, species, and date from the RUN_CAL_USED database.

*PRINT_CALENTRY_SUM_ON_FILE* produces a summary report of all calibration data processing steps completed by date, by instrument from the CAL_ENTRY database.

### Worksheets/Databases

Several worksheets implemented with the LOTUS 123 software on the IBM PC are used. These are backed-up on 5.25 inch floppy diskettes. Each of these will be discussed in detail in Chapter 3.

OCSICyy - Injections into the smog chamber are used as calibration sources. This worksheet/database calculates the chamber concentration from the amount injected, the chamber temperature, the ideal gas law, and compound physical data from a lookup table in the worksheet. A different worksheet is maintained for each year (yy).

CAL - All hydrocarbon calibration sources are compared and "validated" in this worksheet/database. It is listed in Appendix B.

MANmmddyy - "Man"ually performed gas phase titration calibrations for the $NO_x$ and $O_3$ monitors are processed in this worksheet. One worksheet is produced for each calibration identified by date (month, day, year).

MANCALyy - The calibration factors resulting from the MANmmddyy worksheets is analyzed in this worksheet.

## 3

# Calibration

### Approach

All instruments are calibrated at a minimum of two reference levels: a "zero" and a "span" point. The latter is generally near the expected maximum concentration in the experiments. "Zero" air samples are obtained by sampling from a zero air generator or by sampling from a filter specific for the species being monitored. "Span" values are generated from several sources that will be described below. During the programs, different "span" levels are used. These different levels assure that linearity can be checked in final QA procedures, to be discussed in later sections. Several different calibration standard sources, including NBS traceable sources and sources from outside groups, are utilized and compared. Calibrations for most instruments are performed immediately before an experiment. $NO_x$ and $O_3$ monitors are calibrated twice daily. These calibration data are used to adjust the data collected in final data processing steps after the calibration data itself has been processed and reviewed in the context of the entire calibration database for the season.

## NBS-Traceable Sources

### NO and O3 Sources

Two techniques are used to calibrate the chemiluminescent $NO_x$ and $O_3$ monitors. The primary technique is the EPA gas-phase titration method[3] which utilizes a high concentration NO source (NBS-traceable) as the primary standard. Comparison of this primary source with other sources is performed regularly. In one recent study, three of these high concentration sources were compared and found to agree within a few percent of each other. Low concentration sources of NO and $O_3$ are also used to perform span checks more frequently and automatically (AUTOCAL source). Low concentration (<1 ppm) pressurized gas cylinders are used for NO sources, and a generator built into the $O_3$ monitor is used for the $O_3$ AUTOCAL source. These are calibrated and used as transfer standards. Table 2 lists the calibration sources used for $NO_x$.

Table 2. NO Tank Calibration Sources

| Name | Manuf. | Manf. ID | UNC ID | OCS ID |
|---|---|---|---|---|
| NO 46.0 ppm | Matheson | SX-13759 | UNCAB2113 | 94 |
| NO 52.4 ppm | Airco | 1122590 | UNCBC9045 | 178 |
| NO 52.6 ppm | Scott | BAL177 | UNCAB0348 | 179 |
| NO 0.823 ppm | | CC-15860 | | 4 |
| NO 0.288 ppm | | | | 180 |
| NO 0.665 ppm | Airco | CC-15780 | UNCAB2478 | 181 |

The OCS ID heading will be explained below.

## Hydrocarbon Sources

Commercially prepared NBS traceable calibration sources are also used for hydrocarbons. Five different tanks purchased by UNC were used. In addition, three other tanks were borrowed from the Research Triangle Institute (RTI) which is involved in a multiyear intercomparison of commercial hydrocarbon calibration sources. A low concentration tank prepared from diluting a small portion of one of the commercially prepared high concentration tanks was calibrated as a transfer standard for automatic calibration. These calibration sources are listed in Table 3. Another source of hydrocarbon standards was prepared in the chambers by injecting liquid hydrocarbons. These are listed in Table 4. The identities and properties of the species calibrated this way are given in Table 5. All sources were compared and results are described below.

### Table 3. HC Tank and Liquid Calibration Sources

| | | | | |
|---|---|---|---|---|
| NEW AIRCO | Airco | X-3362 | UNCAB2467 | 112 |
| LOW MW (HC) | Scott | AAL11557 | UNCAB2136 | 109 |
| LOW MW (LC) | UNC | NA | NA | 111 |
| HIGH MW | Scott | AAL11551 | UNCAB2139 | 108 |
| RTI- ethylene | | 2H | | 167 |
| RTI- propylene | | 3A | | 168 |
| RTI- propane (in 1985) | | | | 171 |
| 82HCCALMIX | | XA-1336 | | 1 |
| NEWSCOTTCALTANK | | | | 110 |
| LIQ STD 8/14/84 | | NA | | 123 |

### Transfer Standards Created from Primary Sources

For $NO_x$, $O_3$, and hydrocarbons, several sources traceable to NBS are used. These are high concentration tanks for stability and accuracy which require dilution or instrument attenuation adjustment when used. Accurate liquid injections into the smog chamber are also considered as primary standards. Several low concentration NO tanks were purchased as a source for automatic calibrations ("AUTOCAL" sources). A low concentration HC tank was prepared by diluting a portion of the LOW MOLECULAR WEIGHT (high concentration) calibration tank into an empty tank with nitrogen to be used as an AUTOCAL source. AUTOCAL sources do not require a morning operator to be present to change the attenuation settings and are not subject to possible errors from dilution. These calibration sources were intercompared. The RTI tanks were considered absolute because of their extensive comparative analysis history. In the case of the hydrocarbon sources, some judgements resulted in small adjustments to the "validated" concentrations to make all the UNC sources more consistent. The intercomparison procedures result in calibration of the AUTOCAL sources.

## Primary Source Comparison

### NO and O3 Sources

This test is conducted to compare the manufacturers stated analyzed gas concentrations of the NO tanks. Nitrogen oxide tanks are available for use in the EPA Gas Phase Titration method (see description in "Routine $NO_x$ and $O_3$ Calibrations"). Three tanks with NO concentrations of 52.6, 52.4, and 46 ppm (see 2) were diluted

## Table 4. OCS from Injections in Chamber

OFFICIAL CALIBRATION SOURCES FROM INJECTIONS INTO SMOG CHAMBER - 1984

LAST 07-Nov-86

CHAMB 150000 (L) STP VOL: 22.414 (L)

| OCS ID # | SOURCE DATE | SPEC ID # | SPECIE NAME | C # | DENSITY | MW | UL or G | T F | PURITY | CONC UL | CONC G |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 95 | 6/25 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 283.000 | 70.0 | 100% | 2.9679 | NA |
| 96 | 6/25 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 556.000 | 70.0 | 100% | 5.8955 | NA |
| 97 | 6/27 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 463.000 | 70.0 | 100% | 4.9093 | NA |
| 98 | 6/26 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 283.000 | 71.8 | 100% | 2.9780 | NA |
| 99 | 6/26 | 71 | O-XYLENE | 8 | 0.897 | 106.1 | 243.000 | 71.8 | 100% | 2.6530 | NA |
| 100 | 6/19 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 370.500 | 70.0 | 100% | 3.9285 | NA |
| 101 | 6/19 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 282.900 | 70.0 | 100% | 2.9668 | NA |
| 102 | 7/10 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.110 | 70.0 | 92% | NA | 0.5421 |
| 103 | 7/10 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.210 | 70.0 | 92% | NA | 1.0350 |
| 104 | 7/11 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 70.0 | 92% | NA | 0.9463 |
| 105 | 7/11 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 70.0 | 92% | NA | 0.9463 |
| 106 | 7/27 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 70.0 | 92% | NA | 0.9463 |
| 107 | 7/27 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.038 | 70.0 | 92% | NA | 0.1893 |
| 115 | 7/31 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 70.0 | 92% | NA | 0.9463 |
| 116 | 6/28 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 556.000 | 77.3 | 100% | 5.9767 | NA |
| 117 | 6/28 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 283.000 | 77.3 | 100% | 3.0088 | NA |
| 118 | 7/16 | 40 | BENZENE | 6 | 0.878 | 78.11 | | | 100% | 0.0000 | NA |
| 118 | 7/16 | 55 | TOLUENE | 7 | 0.867 | 92.14 | | | 100% | 0.0000 | NA |
| 118 | 7/16 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | | | 100% | 0.0000 | NA |
| 118 | 7/16 | 71 | O-XYLENE | 8 | 0.897 | 106.1 | | | 100% | 0.0000 | NA |
| 118 | 7/16 | 67 | P-XYLENE | 8 | 0.861 | 106.1 | | | 100% | 0.0000 | NA |
| 118 | 7/16 | 89 | STYRENE | 8 | 0.906 | 104.1 | | | 100% | 0.0000 | NA |
| 119 | 7/27 | 82 | 2,2,4-TRIMETHYL | 8 | 0.692 | 114.2 | | | 100% | 0.0000 | NA |
| 120 | 7/27 | 40 | BENZENE | 6 | 0.878 | 78.11 | | | 100% | 0.0000 | NA |
| 123 | 8/14 | 19 | N-PENTANE | 5 | 0.626 | 72.15 | 416.000 | 85.0 | 100% | 2.9875 | NA |
| 123 | 8/14 | 28 | 2-METHYLPENTANE | 6 | 0.653 | 86.18 | 420.000 | 85.0 | 100% | 3.1609 | NA |
| 123 | 8/14 | 42 | 2,3-DIMETHYLPEN | 7 | 0.695 | 100.2 | 372.000 | 85.0 | 100% | 2.9897 | NA |
| 123 | 8/14 | 82 | 2,2,4-TRIMETHYL | 8 | 0.692 | 114.2 | 373.000 | 85.0 | 100% | 2.9925 | NA |
| 123 | 8/14 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 274.000 | 85.0 | 100% | 2.9876 | NA |
| 123 | 8/14 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 276.000 | 85.0 | 100% | 2.9765 | NA |
| 123 | 8/14 | 71 | O-XYLENE | 8 | 0.897 | 106.1 | 239.000 | 85.0 | 100% | 2.6630 | NA |
| 124 | 6/27 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 188.600 | 70.0 | 100% | 1.9779 | NA |
| 125 | 7/13 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.212 | 68.0 | 92% | NA | 1.0384 |
| 126 | 7/13 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.212 | 68.0 | 92% | NA | 1.0384 |

## Table 4, cont.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 127 | | 205 | MEOH | 1 | 0.791 | 32.04 | 224.000 | 70.4 | 100% | 0.8914 | NA |
| 128 | | 205 | MEOH | 1 | 0.791 | 32.04 | 224.000 | 74.0 | 100% | 0.8974 | NA |
| 129 | | 205 | MEOH | 1 | 0.791 | 32.04 | 80.100 | 74.0 | 100% | 0.3209 | NA |
| 130 | | 205 | MEOH | 1 | 0.791 | 32.04 | 74.700 | 75.5 | 100% | 0.3001 | NA |
| 131 | | 205 | MEOH | 1 | 0.791 | 32.04 | 196.700 | 73.0 | 100% | 0.7866 | NA |
| 132 | | 205 | MEOH | 1 | 0.791 | 32.04 | 65.500 | 74.5 | 100% | 0.2627 | NA |
| 133 | 10/7 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 54.0 | 92% | NA | 0.9177 |
| 134 | 10/7 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.097 | 54.0 | 92% | NA | 0.4636 |
| 135 | 10/9 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 55.0 | 92% | NA | 0.9195 |
| 136 | 10/9 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 55.0 | 92% | NA | 0.9195 |
| 137 | 10/16 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.048 | 61.0 | 92% | NA | 0.2325 |
| 138 | 10/16 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.096 | 61.0 | 92% | NA | 0.4651 |
| 140 | 8/25 | 205 | MEOH | 1 | 0.7914 | 32.04 | 74.000 | 66.2 | 100% | 0.2921 | NA |
| 143 | 9/1 | 205 | MEOH | 1 | 0.7914 | 32.04 | 249.000 | 59.0 | 100% | 0.9695 | NA |
| 144 | 9/3 | 205 | MEOH | 1 | 0.7914 | 32.04 | 66.900 | 66.7 | 100% | 0.2644 | NA |
| 147 | 9/17 | 205 | MEOH | 1 | 0.7914 | 32.04 | 151.000 | 45.0 | 100% | 0.5721 | NA |
| 148 | 9/25 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 62.0 | 92% | NA | 0.9320 |
| 159 | 9/5 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 78.0 | 92% | NA | 0.9606 |

## Table 4, cont.

OFFICIAL CALIBRATION SOURCES FROM INJECTIONS INTO SMOG CHAMBER - 1985

LAST 07-Nov-86

CHAMB 150000 (L) STP VOL: 22.414 (L)

| OCS ID # | SOURCE DATE | SPEC ID # | SPECIE NAME | C # | DENSITY | MW | UL or G | T F | PURITY | CONC IF UL | CONC IF GRAMS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 162 | 5/14/85 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 92.000 | 86.0 | 100% | 1.0050 | NA |
| 162 | 5/14/85 | 40 | BENZENE | 6 | 0.878 | 78.11 | 45.000 | 86.0 | 100% | 0.5033 | NA |
| 162 | 5/14/85 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 185.000 | 86.0 | 100% | 1.9988 | NA |
| 162 | 5/14/85 | 82 | 2,2,4-TRIMETHY | 8 | 0.692 | 114.2 | 240.000 | 86.0 | 100% | 1.9290 | NA |
| 163 | 5/17/85 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 100.000 | 72.0 | 100% | 1.0643 | NA |
| 163 | 5/17/85 | 40 | BENZENE | 6 | 0.878 | 78.11 | 50.000 | 72.0 | 100% | 0.5449 | NA |
| 163 | 5/17/85 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 200.000 | 72.0 | 100% | 2.1054 | NA |
| 163 | 5/17/85 | 82 | 2,2,4-TRIMETHY | 8 | 0.692 | 114.2 | 300.000 | 72.0 | 100% | 2.3494 | NA |
| 164 | 5/20/85 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.201 | 82.0 | 95% | NA | 1.0461 |
| 165 | 5/22/85 | 82 | 2,2,4-TRIMETHY | 8 | 0.692 | 114.2 | 100.000 | 80.0 | 100% | 0.7949 | NA |
| 165 | 5/22/85 | 40 | BENZENE | 6 | 0.878 | 78.11 | 150.000 | 80.0 | 100% | 1.6593 | NA |
| 165 | 5/22/85 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 200.000 | 80.0 | 100% | 2.1607 | NA |
| 165 | 5/22/85 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 400.000 | 80.0 | 100% | 4.2741 | NA |
| 165 | 5/22/85 | 71 | O-XYLENE | 8 | 0.897 | 106.1 | 500.000 | 80.0 | 100% | 5.5431 | NA |
| 165 | 5/22/85 | 78 | 1,2,4-t*BENZEN | 9 | 0.876 | 120.2 | 500.000 | 80.0 | 100% | 5.3791 | NA |
| 166 | 5/24/85 | 82 | 2,2,4-TRIMETHY | 8 | 0.692 | 114.2 | 100.000 | 65.0 | 100% | 0.7728 | NA |
| 166 | 5/24/85 | 40 | BENZENE | 6 | 0.878 | 78.11 | 150.000 | 65.0 | 100% | 1.6132 | NA |
| 166 | 5/24/85 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 200.000 | 65.0 | 100% | 2.1006 | NA |
| 166 | 5/24/85 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 400.000 | 65.0 | 100% | 4.1553 | NA |
| 166 | 5/24/85 | 71 | O-XYLENE | 8 | 0.897 | 106.1 | 500.000 | 65.0 | 100% | 5.3889 | NA |
| 173 | 6/21/85 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.148 | 59.0 | 95% | NA | 0.7376 |
| 174 | 6/21/85 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.295 | 59.0 | 95% | NA | 1.4701 |
| 176 | 8/8/85 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.192 | 82.0 | 95% | NA | 0.9993 |
| 177 | 8/8/85 | 40 | BENZENE | 6 | 0.878 | 78.11 | 150.000 | 83.0 | 100% | 1.6686 | NA |
| 177 | 8/8/85 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 200.000 | 83.0 | 100% | 2.1727 | NA |
| 177 | 8/8/85 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 400.000 | 83.0 | 100% | 4.2979 | NA |
| 177 | 8/8/85 | 71 | O-XYLENE | 8 | 0.897 | 106.1 | 500.000 | 83.0 | 100% | 5.5739 | NA |
| 177 | 8/8/85 | 82 | 2,2,4-TRIMETHY | 8 | 0.692 | 114.2 | 100.000 | 83.0 | 100% | 0.7993 | NA |
| 177 | 8/8/85 | 78 | 1,2,4-t*BENZEN | 9 | 0.876 | 120.2 | 500.000 | 83.0 | 100% | 5.4091 | NA |
| 186 | 8/26/85 | 82 | 2,2,4-TRIMETHY | 8 | 0.692 | 114.2 | 100.000 | 80.0 | 100% | 0.7949 | NA |
| 186 | 8/26/85 | 40 | BENZENE | 6 | 0.878 | 78.11 | 150.000 | 80.0 | 100% | 1.6593 | NA |
| 186 | 8/26/85 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 200.000 | 80.0 | 100% | 2.1607 | NA |
| 186 | 8/26/85 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 400.000 | 80.0 | 100% | 4.2741 | NA |

## Table 4, cont.

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 186 | 8/26/85 | 71 | O-XYLENE | 8 | 0.897 | 106.1 | 500.000 | 80.0 | 100% | 5.5431 | NA |
| 186 | 8/26/85 | 78 | 1,2,4-tmBENZEN | 9 | 0.876 | 120.2 | 500.000 | 80.0 | 100% | 5.3791 | NA |
| 187 | 12/9/85 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.197 | 78.0 | 95% | NA | 1.0177 |
| 188 | 12/9/85 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.096 | 78.0 | 95% | NA | 0.4959 |
| 189 | 9/30/85 | 139 | HCHO | 1 | 0.815 | 30.05 | 0.197 | 65.0 | 95% | NA | 0.9931 |
| 190 | 8/29/85 | 55 | TOLUENE | 7 | 0.867 | 92.14 | 69.500 | 65.0 | 100% | 0.7300 | NA |
| 191 | 8/29/85 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 70.700 | 65.0 | 100% | 0.7344 | NA |
| 192 | 8/15/85 | 78 | 1,2,4-tmBENZEN | 9 | 0.876 | 120.2 | 87.000 | 62.2 | 100% | 0.9051 | NA |
| 193 | 8/15/85 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 87.000 | 62.2 | 100% | 0.8989 | NA |
| 194 | 8/12/85 | 68 | M-XYLENE | 8 | 0.864 | 106.1 | 87.500 | 63.0 | 100% | 0.9055 | NA |
| 195 | 8/12/85 | 78 | 1,2,4-tmBENZEN | 9 | 0.876 | 120.2 | 86.900 | 62.0 | 100% | 0.9037 | NA |

## Table 5. Species ID numbers and Properties

```
ID       NAME        #  DENS    MW  PURITY

 19 N-PENTANE      5  0.626 72.15     100%
 28 2-METHYLPENTANE 6  0.653 86.18     100%
 40 BENZENE        6  0.878 78.11     100%
 42 2,3-DIMETHYLPEN 7  0.695 100.2     100%
 55 TOLUENE        7  0.867 92.14     100%
 60 N-OXTANE       8  0.703 114.2     100%
 67 P-XYLENE       8  0.861 106.1     100%
 68 M-XYLENE       8  0.864 106.1     100%
 71 O-XYLENE       8  0.897 106.1     100%
 82 2,2,4-TRIMETHYL 8  0.692 114.2     100%
 89 STYRENE        8  0.906 104.1     100%
139 HCHO           1  0.815 30.05      92%
205 MEOH           1 0.7914 32.04     100%
```

```
ID       NAME       #  DENS    MW  PURITY

 19 N-PENTANE     5  0.626 72.15     100%
 28 2-METHYLPENTAN 6  0.653 86.18     100%
 40 BENZENE       6  0.878 78.11     100%
 42 2,3-DIMETHYLPE 7  0.695 100.2     100%
 55 TOLUENE       7  0.867 92.14     100%
 60 N-OXTANE      8  0.703 114.2     100%
 67 P-XYLENE      8  0.861 106.1     100%
 68 M-XYLENE      8  0.864 106.1     100%
 71 O-XYLENE      8  0.897 106.1     100%
 78 1,2,4-tmBENZEN 9  0.876 120.2     100%
 82 2,2,4-TRIMETHY 8  0.692 114.2     100%
 89 STYRENE       8  0.906 104.1     100%
139 HCHO          1  0.815 30.05      95%
205 MEOH          1 0.7914 32.04     100%
```

with clean air (zero air generator) to concentrations of approximately 0.2, 0.6 and 0.8 ppm. The exact calculated concentrations were determined by flow measurements with soap-bubble meters for the air and NO. The measured concentrations were plotted against the calculated concentration. All data were fit to a straight line with the least-squares method. The data is plotted in Figure 1 and is shown in Table 6. Agreement between the sources is excellent. The values assigned to these tanks determine the absolute accuracy of our reported $NO_x$ and $O_3$ data.

### Hydrocarbon Sources

Because there is much less of a distinction between primary and working sources for hydrocarbons than for $NO_x$ and $O_3$ sources, the comparison of primary hydrocarbon sources will be discussed below in the next section on transfer standards.

## Transfer Calibration to working "AUTOCAL" Sources

### NOx and O3 Calibration Sources

Experience and analysis of past calibration data indicates that calibration factors estimated from the results of the "manually" performed gas-phase titration method vary more than the calibration factors obtained from the automatic span checks using low concentration sources. But when the manual values are averaged, they yield the same results. The low concentration sources are convenient, but require careful characterization, since their concentration decreases slightly during the run season. Our experience and analysis also shows that the instruments are more stable if the zero and span settings are not adjusted. Therefore, the following strategy is followed to maximize the quality of the data from these instruments.

The $NO_x$ and $O_3$ instruments are not adjusted after the initial start-up at the beginning of the experimental season. Manual gas-phase titration calibrations are performed to estimate calibration factors for the instruments throughout the experimental season. The low concentration sources are used twice a day. The responses are plotted for the entire run season to establish a decay rate for the low concentration sources. The manual calibration factors establish the concentrations of these low concentration sources at the beginning of the season. The calibrated responses from the low concentration sources are then used to calibrate the instruments. The flowchart illustrating the procedures associated with the transfer of $NO_x$ and $O_3$ calibrations is shown in Figure 2.

### Manual Gas Phase Titration

The manual Gas Phase Titration calibrations are performed occasionally through-

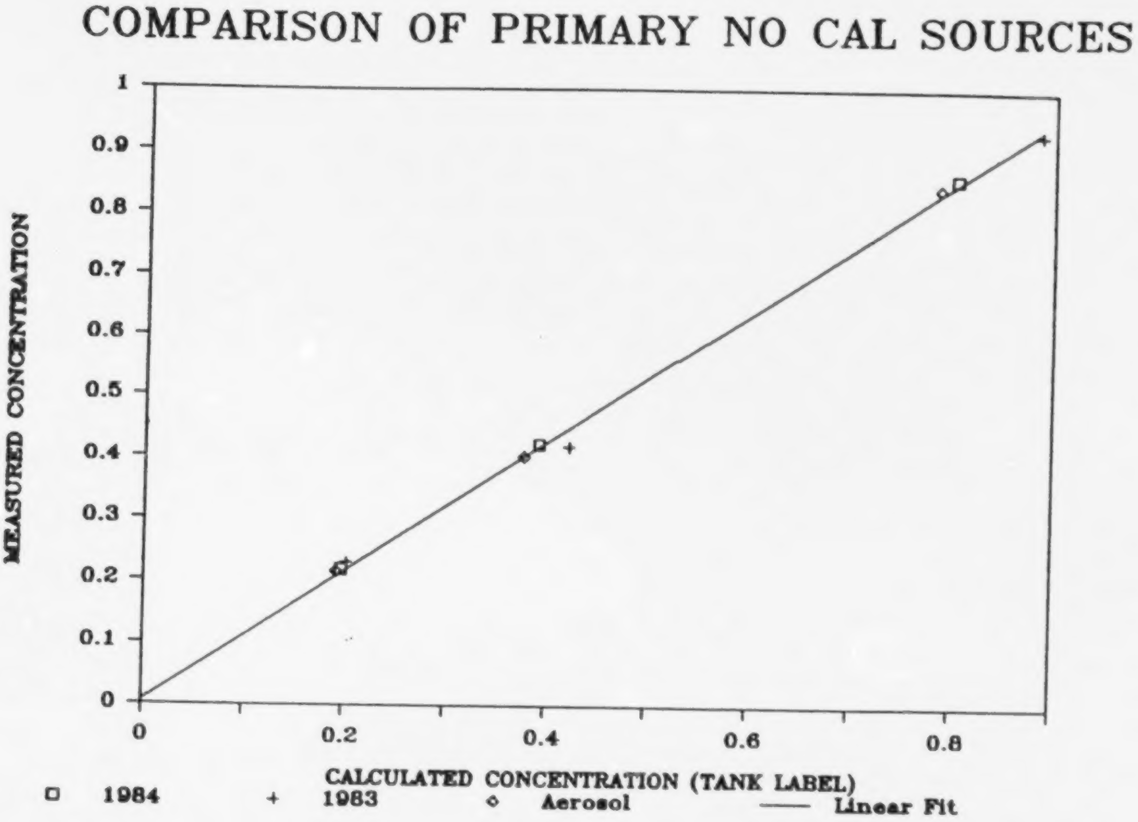


Figure 1. Comparison of Primary NO Calibration Sources

## Table 6. Comparison of Primary NO Calibration Sources

| TANK | CALC. CONC. | ESTIMATE CONC. | MEASURED CONC. | DELTA CONC. | PERCENT |
|---|---|---|---|---|---|
| 1 | 0.197 | 0.213 | 0.218 | 0.005 | 2.3% |
| 1984 | 0.392 | 0.418 | 0.423 | 0.005 | 1.2% |
| 52.4 ppm | 0.803 | 0.849 | 0.855 | 0.006 | 0.7% |
| 2 | 0.202 | 0.218 | 0.229 | 0.011 | 4.8% |
| 1983 | 0.422 | 0.449 | 0.419 | -0.030 | 6.7% |
| 46 ppm | 0.886 | 0.936 | 0.930 | -0.006 | 0.7% |
| 3 | 0.192 | 0.208 | 0.215 | 0.007 | 3.4% |
| Aerosol Project | 0.377 | 0.402 | 0.403 | 0.001 | 0.2% |
| 52.6 ppm | 0.786 | 0.831 | 0.840 | 0.009 | 1.0% |
|  |  |  |  | ave | 2.3% |

out the season as discussed above. The technique is the EPA reference method as described in the CFR[3].

This calibration technique is based upon the rapid gas phase reaction between NO and $O_3$ to produce stoichiometric quantities of $NO_2$. The quantitative nature of this reaction is such that when the NO concentration is known (primary calibration standard), the concentration of $NO_2$ and $O_3$ can be determined. $O_3$ is added to excess NO in a dynamic calibration system, and the $NO/NO_x/NO_2$ analyzer is used as an indicator of changes in NO concentration. Upon the addition of $O_3$, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of $NO_2$ produced and $O_3$ consumed.

### *Calibration Factors from Primary Sources*

Each "manual" calibration is processed with the aid of an electronic form implemented with LOTUS 123 on an IBM PC called `MANCALSH.WKS` in Figure 2 (see figure Figure 3. Information is transfered from the paper form filled in during the gas phase titration calibration procedure. The results of each manual calibration are inspected for notes of problems that were encountered, such as odd or unstable readings. The electronic form assures that the calculations are performed correctly. The completed form is printed out and the file is saved on diskette and backed up to another diskette, thus resulting in at least four sources of the calibration data.

Another LOTUS 123 electronic form and database is used to collect the final calibration factors for all calibrations (called MANCAL.WKS in Figure 2). Output from this worksheet is shown in Figure 4 and Figure 5. The data are fitted with a straight line using a least-squares method. The data and the straight line fit are plotted as a function of date; these are shown in Figure 6 and Figure 7. The plots are used to visually inspect the data for trends and large variations. If necessary, the individual calculation electronic forms can be inspected for errors in transfering data. The original paper form can also be examined. If there are problems, the data in the database may be invalidated.

If no trend is observed, the calibration factors are simply averaged for the season to estimate the true calibration factor for the instrument. Analysis of manual calibrations performed over many years by many people show variation by human error but usually no trend. If a trend were observed, the calibration factor for a particular time of interest would be estimated by a least-squares estimate through the calibration data points.

### *Calibration of AUTOCAL Sources - Transfer Standards*

The response and zero data from the AUTOCAL procedures (NO, $NO_X$, and $O_3$) are plotted and listed using a DATATRIEVE database. The first QA step is to investigate the large variations or odd values. Sometimes a calibration was not conducted and regular experimental data was processed as a calibration. A regression is calculated to estimate the decay rate and to estimate the intercept (correct response) at the beginning of the season or start of a new span check tank. The average (or if a trend was observed, the appropriate time specific) manual calibration factor is used to calculate the true concentrations of the AUTOCAL calibration sources from the responses at these times (see bottom of Figure 4and 5and discussion of routine $NO_X$ and $O_3$ calibrations for final report of AUTOCAL calibration factors).

## Hydrocarbon Sources

A procedure similar to that performed for the different NO and $O_3$ calibration sources was performed for the hydrocarbon calibration sources. The comparison was far more complex because of the large number of species and different sources utilized. Five commercially prepared tanks purchased by UNC were compared and analyzed. Two additional well-characterized (several years history) tanks which are part of an on-going study of commercial HC calibration sources were borrowed from RTI in 1984 and again in 1985 plus an additional third tank. A low concentration tank was prepared from one of the purchased tanks. These were also compared. Liquid injections into the smog chamber used as calibration sources were also compared with these tank sources. The low concentration tank was calibrated as a working AUTOCAL source. All of the tanks, however, were used occassionally for calibration. A list of the sources that were compared is given in Table 7.

The borrowed RTI tanks were considered to be an absolute standard. The values of the other calibration sources were "analyzed" based on the RTI tanks as the primary standard. In most cases the final analyzed values for all compounds for all sources were within a few percent of the manufacturers reported concentrations and the liquid injected sources from the UNC chamber. Only one compound (2-methyl-1,3-butadiene ) was outside of the manufacturers stated uncertainty. This compound is not important to the present research program.

The intercomparisons of the HC sources was performed with a LOTUS 123 spreadsheet on an IBM PC. The spreadsheet is listed in Appendix B.

Table 8 shows the agreement with the manufacturers analysis after "validating" the tanks with the RTI NBS-traceable tanks (see Table 7). For each tank, the average and standard deviation of the ratio of the "validated" to manufacturers stated

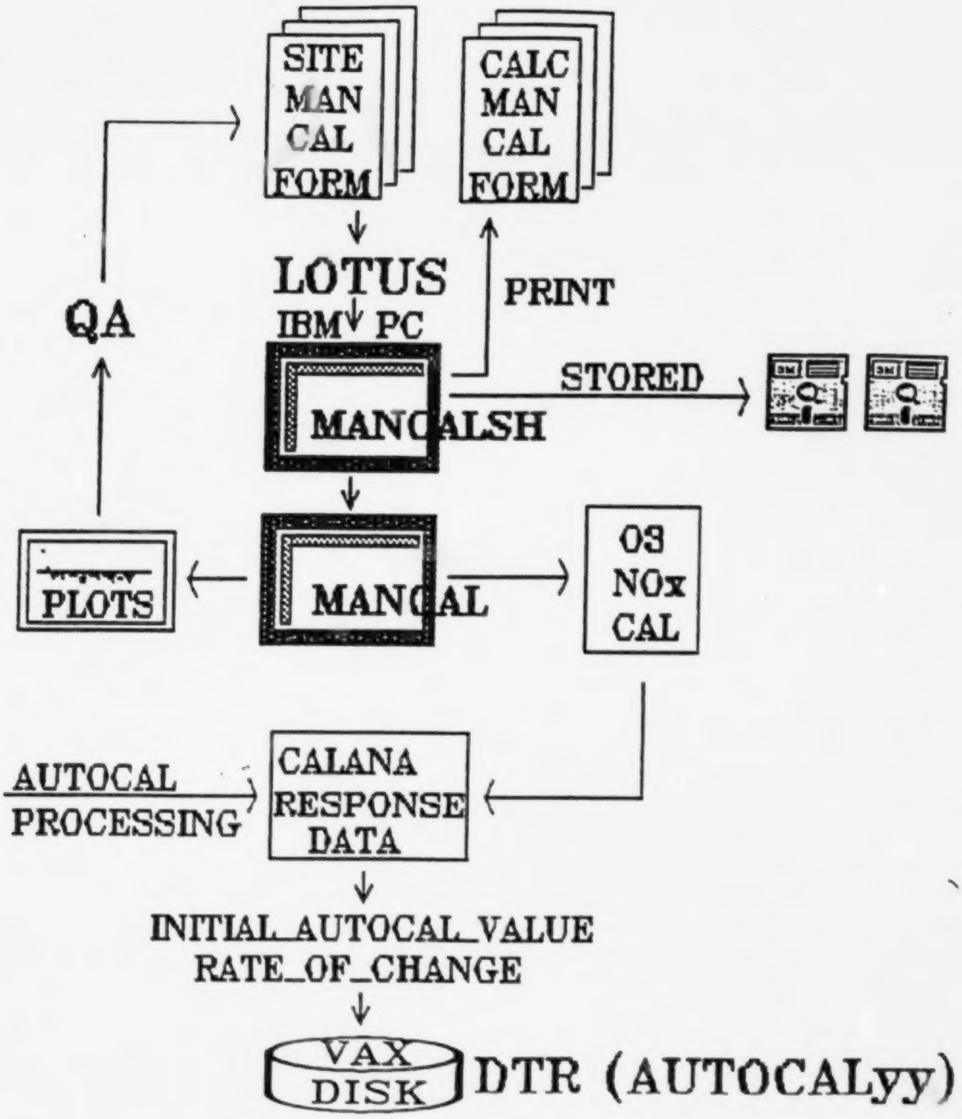

SITE MAN CAL FORM
CALC MAN CAL FORM
LOTUS
IBM PC
PRINT
QA
STORED
MANCALSH
PLOTS
MANCAL
O3 NOx CAL
AUTOCAL PROCESSING
CALANA RESPONSE DATA
INITIAL_AUTOCAL_VALUE
RATE_OF_CHANGE
VAX DISK
DTR (AUTOCALyy)

**Figure 2.** $NO_x$ and $O_3$ Cal Processing Flowchart

```
NO-O3 Calibration Data Sheet         DATE 8/6/85      NAME Suedbeck
                                          --------         -----------------------
Air Flow:
 volume   0.485     time    0.221    0.223    0.222    0.223    0.221      av: 0.22200
        --------          -------  -------  -------  -------  -------          --------
                                                              air flow =       2.18468
                                                                               --------
NO Cal Tank Flow(tank and O3 turned on __30_ min before flow rate measurements)
 volume    0.01      time    0.361    0.361    0.359    0.360    0.361      av: 0.36040
        --------           -------  -------  -------  -------  -------          --------
                                                              NO flow =        0.02775
                                                                               --------
                                          !-         NO Flow        -!
Predicted NO:    tnk conc 52.453          !          0.02775         !         0.65783
                          --------    x   ! ------------------------ !    =    --------
                                          !          2.21243         !
                                          !_     NO + Air Flow      _!

                                                  0.01254
                                                  --------
              ZERO READING !ZERO POT SETTING
                                                     SPAN READING !SPAN POT SETTING
             --------------!---------------
             before/ after! !before/ after!         --------------!---------------
  NO  (1)   -0.015         !    214                 before/ after! !before/ after!
             ------- -------!------- -------   (2)    0.586        !    604
  NO2 (1)   -0.009         !     35                 ------- -------!------- -------
             ------- -------!------- -------   (2)   -0.002        !    572
  NOX (1)   -0.018         !    181                 ------- -------!------- -------
             ------- -------!------- -------   (2)    0.642        !    714
  O3  (2)    0.001         !      0                 ------- -------!------- -------
             ------- -------!------- -------                       !    230
             ! enter NA if no adjustment made to pot settings      !------- -------
             (1) zero air with H2O (purafil)
                                                    (2) with NO added
O3 SLIDE OUT AND TITRATION BEGINS!

NO during titration       0.2133             delta  0.3724
                          --------                  --------

NO2 during titration      0.4112             delta  0.4130
                          --------                  --------

Ozone during titration    0.0665   (measure at outlet)
                          --------

                                          !-         Air Flow       -!
Ozone with NO TURNED OFF 0.4153           !          2.18468         !
(wait for stable value)  --------     x   ! ------------------------ !    =    0.41009
(measure at inlet)                        !                          !         --------
                         0.4162           !          2.21243         !
(measure at outlet)      --------         !_     NO + Air Flow      _!
                                                     0.98746
                                                     --------
If difference between inlet and outlet is more than a few ppb, wait longer.

Ozone (delta corrected for NO dilution):  delta 0.34363
                                                --------
'O3 rotoball setting     _____3 Ethylene pres.    ____15 O2 pres.    ____20
```

Figure 3. LOTUS Spreadsheet for Manual Cal Processing

```
SPAN CALIBRATION FACTORS

  NO     1.0944   = predicted NO / (NO span - NO zero)
        --------

  NO2    0.9869   = (delta NO x NO span cal factor) / delta NO2
        --------

  NOX    1.0079   = (predicted NO + ((NO2 span - NO2 zero) * NO2 cal factor)) /
        --------        (NOx span - NOx zero)

  O3     1.1861   = (delta NO x NO span cal factor) / delta O3
        --------
*****************************************************************************
IF instrument adjustments are to be made - these are desired span values
ADJUSTMENT ORDER: 1) ZEROS, 2) NO SPAN, 3) NOX SPAN, 4) NO2 SPAN, 3) O3 SPAN

NO span value      = predicted NO + NO zero

NOx span value     = (predicted NO + ((NO2 span - NO2 zero) * NO2 correction)) +
                          NOx zero

NO2 span value     = (delta NO x NO span correction) + NO2 zero
                             (should be 1.0 now)      (should be 0.0)

O3 span value      = (((O3 value during titration x O3 span correction) +
                         (delta NO x NO span correction)) x DCF) + O3 zero
                               (should be 1.0 now)          (should be 0.0)

                               :-        NO + Air Flow    -:
                               :           2.21243          :
               DCF     =       : -------------------------- :     =     1.01270
                               :           2.18468          :           --------
                               :_          Air Flow        _:

O3 rotoball setting   ______

Time that O3  instrument adjustments made or NA   ______

Time that NOx instrument adjustments made or NA   ______
*****************************************************************************
          AUTO ZERO                      AUTO SPAN DATA             AUTO SPAN & CORR
                                         TANK     AB2478            TANK
                                         SPAN     CORRECTED         SPAN     CORRECTED
          -------                        -------- -------           -------  -------
 NO  (1)  -0.0202                   (2)  0.60751  0.68706      (2)
          -------                        -------                    -------
NO2  (1)  -0.0068                   (2)  0.00023  0.00693      (2)
          -------                        -------- 0.69400           -------
NOX  (1)  -0.0217                   (2)  0.66927  0.69651      (2)
          -------                        -------                    -------
 O3  (1)  0.00088                   (3)  0.10582  0.12446      (3)
          -------                        -------                    -------
          (1) regular auto zero    (2) be sure to check for excess flow rate
          (3) regular auto span generator
```

**Figure 3, cont.** LOTUS Spreadsheet for Manual Cal Processing.

```
MANUAL CALIBRATIONS

        21-May-85  - last update

 52.4528 ppm NO Tank
                              NO                                  NOx                                 O3
                  ----------------------------------  ----------------------------------  ----------------------------------
   Cal    day zero    real      delta       real/        real      delta       real/        real      delta       real/
  Date   02-Jul-84             response    response               response    response               response    response

02-Jul-84        0    0.7482    0.7710     0.9704       0.7521    0.8170      0.9205       0.2640    0.2344      1.1260
10-Jul-84        8    0.7698    0.8360     0.9208       0.7707    0.8810      0.8747       0.2385    0.2403      0.9926
16-Jul-84       14   0.78355    0.8540     0.9175       0.7836    0.9000      0.8706       0.2340    0.2520      0.9284
18-Jul-84       16                         0.9515
18-Jul-84       16                         0.9615
18-Jul-84       16                         0.9443
29-Aug-84       58    0.7835    0.8430     0.9294       0.7835    0.8840      0.8863       0.2172    0.2387      0.9100


LEAST SQUARES FOR SPAN NO
     N        X          Y        N*X        N*Y      YDEV2    est y       X2         Y2         XY rel std dev
-----------------------------------------------------------------------------------------------------------------------
     1        0 0.97042801          0 0.97042801 0.00079638   0.9491        0 0.94173053          0      1.13
     1        8 0.92080143          8 0.92080143 0.00045822   0.9461       64 0.84787528 7.36641148     -1.34
     1       14 0.91750585         14 0.91750585 0.00061018   0.9438      196 0.84181699 12.8450819     -1.39
     1       16     0.9515         16     0.9515 0.00008634   0.9431      256 0.90535225     15.224      0.45
     1       16     0.9615         16     0.9615 0.00037219   0.9431      256 0.92448225     15.384      0.98
     1       16     0.9443         16     0.9443 0.00000437   0.9431      256 0.89170249    15.1088      0.07
     1       58 0.92941874         58 0.92941874 0.00016355   0.9273     3364 0.86381919 53.9062870      0.11
-----------------------------------------------------------------------------------------------------------------------
     7                            128 6.59545404 0.00249127              4392 6.21677899 119.834580

                    AVE CAL:   0.94220772                  SD:       0.01886519 SLOPE:     -3.744E-04
                    XBAR:      18.2857142                                       INTER:     0.94905347
                                                                                R2:        0.11541280

LEAST SQUARES FOR SPAN NOx
     N        X          Y        N*X        N*Y      YDEV2    est y       X2         Y2         XY rel std dev
-----------------------------------------------------------------------------------------------------------------------
     1        0 0.92050183          0 0.92050183 0.00047114   0.8925        0 0.84732363          0      0.49
     1        8 0.87474460          8 0.87474460 0.00455127   0.8907       64 0.76517812 6.99795686     -0.28
     1       14 0.87061111         14 0.87061111 0.00512607   0.8894      196 0.75796370 12.1885555     -0.33
     1       58 0.88631221         58 0.88631221 0.00312430   0.8796     3364 0.78554934 51.4061085      0.12
-----------------------------------------------------------------------------------------------------------------------
     4                             80 3.55216977 0.01327279              3624 3.15601481 70.5926210

                    AVE CAL:   0.88804244                  SD:       0.05760381 SLOPE:     -2.227E-04
                    XBAR:              20                                       INTER:     0.89249673
                                                                                R2:        0.06530589
```

Figure 4. LOTUS Analysis Spreadsheet of Manual Cal 1984

```
LEAST SQUARES FOR SPAN O3
       N          X            Y        N*X         N*Y       YDEV2    est y        X2          Y2          XY rel std dev
------------------------------------------------------------------------------------------------------------------------
       1          0 1.12601851            0 1.12601851 0.03378640   1.0428           0 1.26791769           0       0.86
       1          8 0.99263298            8 0.99263298 0.00254270   1.0214          64 0.98532023 7.94106384      -0.30
       1         14 0.92837585           14 0.92837585 0.00019132   1.0053         196 0.86188173 12.9972620      -0.79
       1         58 0.91000502           58 0.91000502 0.00103701   0.8875        3364 0.82810915 52.7802916       0.23
------------------------------------------------------------------------------------------------------------------------
       4                                 80 3.95703238 0.03755744                 3624 3.94322881 73.7186174

                         AVE CAL:   0.98925809                  SD:          0.09689872 SLOPE:     -2.679E-03
                         XBAR:         20.0000                                          INTER:     1.04283546
                                                                                        R2:        0.50605026

AVE CAL:   Auto Tank 1 : 6/21 to 9/1                                   Auto Tank 2 : 9/1 to 10/16

--------   ---------------------------                             ----------------------------
   NO      response1 CAL VALUE             decay*                   response2 CAL VALUE            decay*
 0.94221    0.30515    0.28751             -4.485E-05                 0.70602    0.66522           -5.687E-04

                                       0.53% agreement                                         -0.42% agreement
  NOx     response1 CAL VALUE              decay*                  response2 CAL VALUE            decay*
 0.88804    0.32207    0.28601             -5.304E-05                 0.75224    0.66802           -3.688E-04

           Auto Cal Gen : 5/30 to 11/6

          ---------------------------
  O3       response CAL VALUE              decay*
 0.98926    0.12218    0.12087             -7.179E-05


response1 -response value for 21-JUN-84 determined from least squares regression of response data

response2 -response value for 1-SEP-84 determined from least squares regression of response data

decay*    -from least squares regression of response data

CAL VALUE -VALUE ENTERED INTO AUTOCAL DATABASE TO GENERATE DAILY CAL FACTORS
```

**Figure 4, cont.** LOTUS Analysis Spreadsheet Manual Cal

```
MANUAL CALIBRATIONS            1985

        07-Nov-86  - last update

  52.4528 ppm NO Tank

                         NO        NO2       NOx       O3
 Cal       day zero  --------- --------- --------- ---------
 Date     01-May-85 cal factor cal factor cal factor cal factor

09-May-85        8    0.9478    0.9567    0.8694    1.2244
30-May-85       29    0.9551    0.9366    0.8790    1.0763
05-Jun-85       35    0.9863    0.9737    0.9062    1.1207
11-Jun-85       41    0.9679    0.9827    0.8942    1.2554
18-Jun-85       48    1.0120    0.9886    0.9308    1.2427
24-Jun-85       54    0.9640    0.9767    0.8863    1.2909
27-Jun-85       57    0.9559    0.9925    0.8785        NA
02-Jul-85       62    1.0059    1.0491    0.9229    1.2772
12-Jul-85       72    1.0502    1.0629    0.9650    1.2179
06-Aug-85       97    1.0944    0.9869    1.0079    1.1861
09-Aug-85      100    1.0232    1.0284    0.9433    1.1883
22-Aug-85      113    0.9574    0.9729    0.8786    1.1330
09-Sep-85      131    1.0281    0.9812    0.9428    1.1288
20-Sep-85      142    0.9838    1.0424    0.9058    1.2246
27-Sep-85      149    1.0052     0.973    0.9243    1.1341
04-Oct-85      156    0.9910    0.9669    0.9105    1.1480


LEAST SQUARES FOR SPAN NO
       N         X         Y       N*X       N*Y      YDEV2    est y          X2         Y2          XY rel std dev
---------------------------------------------------------------------------------------------------------------------
       1         8    0.9478         8    0.9478 0.00227648    0.9737         64 0.89832484      7.5824      -0.67
       1        29    0.9551        29    0.9551 0.00163317    0.9800        841 0.91221601     27.6979      -0.64
       1        35    0.9863        35    0.9863 0.00008487    0.9818       1225 0.97278769     34.5205       0.12
       1        41    0.9679        41    0.9679 0.00076245    0.9836       1681 0.93683041     39.6839      -0.40
       1        48     1.012        48     1.012 0.00027183    0.9857       2304   1.024144      48.576       0.68
       1        54     0.964        54     0.964 0.00099303    0.9875       2916   0.929296      52.056      -0.61
       1        57    0.9559        57    0.9559 0.00156915    0.9884       3249 0.91374481     54.4863      -0.84
       1        62    1.0059        62    1.0059 0.00010790    0.9899       3844 1.01183481     62.3658       0.41
       1        72    1.0502        72    1.0502 0.00299072    0.9929       5184 1.10292004     75.6144       1.48
       1        97    1.0944        97    1.0944 0.00977873    1.0003       9409 1.19771136    106.1568       2.43
       1       100    1.0232       100    1.0232 0.00076659    1.0012      10000 1.04693824      102.32       0.57
       1       113    0.9574       113    0.9574 0.00145256    1.0051      12769 0.91661476    108.1862      -1.23
       1       131    1.0281       131    1.0281 0.00106194    1.0105      17161 1.05698961    134.6811       0.45
       1       142    0.9838       142    0.9838 0.00013718    1.0138      20164 0.96786244    139.6996      -0.78
       1       149    1.0052       149    1.0052 0.00009384    1.0159      22201 1.01042704    149.7748      -0.28
       1       156     0.991       156     0.991 0.00002036    1.0180      24336   0.982081     154.596      -0.70
---------------------------------------------------------------------------------------------------------------------
      16                          1294   15.9282 0.02400085              137348 15.8807230   1297.9977

                   AVE CAL:    0.9955125                   SD:       0.03873052 SLOPE:        3.00E-04
                   XBAR:          80.875                                        INTER:         0.97126
                                                                                R2:              0.122
```

Figure 5. LOTUS Analysis Spreadsheet of Manual Cal

```
LEAST SQUARES FOR SPAN NO2
     N        X          Y        N*X        N*Y      YDEV2     est y        X2        Y2          XY rel std dev
-------------------------------------------------------------------------------------------------------------------
     1        8     0.9567          8     0.9567 0.00119889    0.9800        64 0.91527489     7.6536     -0.68
     1       29     0.9366         29     0.9366 0.00299482    0.9833       841 0.87721956    27.1614     -1.37
     1       35     0.9737         35     0.9737 0.00031064    0.9842      1225 0.94809169    34.0795     -0.31
     1       41     0.9827         41     0.9827 0.00007439    0.9852      1681 0.96569929    40.2907     -0.07
     1       48     0.9886         48     0.9886 0.00000742    0.9862      2304 0.97732996    47.4528      0.07
     1       54     0.9767         54     0.9767 0.00021389    0.9872      2916 0.95394289    52.7418     -0.31
     1       57     0.9825         57     0.9825 0.00007788    0.9876      3249 0.96530625    56.0025     -0.15
     1       62     1.0491         62     1.0491 0.00333795    0.9884      3844 1.10061081    65.0442      1.77
     1       72     1.0629         72     1.0629 0.00512298    0.9900      5184 1.12975641    76.5288      2.13
     1       97     0.9869         97     0.9869 0.00001958    0.9938      9409 0.97397161    95.7293     -0.20
     1      100     1.0284        100     1.0284 0.00137455    0.9943     10000 1.05760656     102.84      1.00
     1      113     0.9729        113     0.9729 0.00033948    0.9963     12769 0.94653441   109.9377     -0.68
     1      131     0.9812        131     0.9812 0.00010251    0.9991     17161 0.96275344   128.5372     -0.52
     1      142     1.0424        142     1.0424 0.00260865    1.0008     20164 1.08659776   148.0208      1.22
     1      149      0.973        149      0.973 0.00033580    1.0019     22201   0.946729    144.977     -0.84
     1      156     0.9669        156     0.9669 0.00059658    1.0029     24336 0.93489561   150.8364     -1.05
-------------------------------------------------------------------------------------------------------------------
    16                           1294    15.8612 0.01871605             137348 15.7423201  1287.8337

                    AVE CAL:     0.991325                  SD:        0.03420165 SLOPE:        1.55E-04
                    XBAR:          80.875                                        INTER:         0.97881
                                                                                 R2:              0.042
                                                                                 AVE:           0.99133
```

```
LEAST SQUARES FOR SPAN NOx
     N        X          Y        N*X        N*Y      YDEV2     est y        X2        Y2          XY rel std dev
-------------------------------------------------------------------------------------------------------------------
     1        8     0.8694          8     0.8694 0.00211082    0.8954        64 0.75585636     6.9552     -0.72
     1       29      0.879         29      0.879 0.00132086    0.9011       841   0.772641     25.491     -0.62
     1       35     0.9062         35     0.9062 0.00008360    0.9028      1225 0.82119844     31.717      0.10
     1       41     0.8942         41     0.8942 0.00044705    0.9044      1681 0.79959364    36.6622     -0.29
     1       48     0.9308         48     0.9308 0.00023889    0.9063      2304 0.86638864    44.6784      0.68
     1       54     0.8863         54     0.8863 0.00084353    0.9080      2916 0.78552769    47.8602     -0.60
     1       57     0.8785         57     0.8785 0.00135746    0.9088      3249 0.77176225    50.0745     -0.85
     1       62     0.9229         62     0.9229 0.00005709    0.9102      3844 0.85174441    57.2198      0.35
     1       72      0.965         72      0.965 0.00246574    0.9129      5184   0.931225      69.48      1.45
     1       97     1.0079         97     1.0079 0.00856665    0.9198      9409 1.01586241    97.7663      2.46
     1      100     0.9433        100     0.9433 0.00078155    0.9206     10000 0.88981489      94.33      0.63
     1      113     0.8786        113     0.8786 0.00135010    0.9241     12769 0.77193796    99.2818     -1.27
     1      131     0.9428        131     0.9428 0.00075384    0.9291     17161 0.88887184   123.5068      0.38
     1      142     0.9058        142     0.9058 0.00009108    0.9321     20164 0.82047364   128.6236     -0.73
     1      149     0.9243        149     0.9243 0.00008021    0.9340     22201 0.85433049   137.7207     -0.27
     1      156     0.9105        156     0.9105 0.00002346    0.9359     24336 0.82901025    142.038     -0.71
-------------------------------------------------------------------------------------------------------------------
    16                           1294    14.6455 0.02057201             137348 13.4262389  1193.4055

                  , AVE CAL:   0.91534375                  SD:        0.03585737 SLOPE:        2.74E-04
                    XBAR:          80.875                                        INTER:         0.89320
                                                                                 R2:              0.119
```

**Figure 5, cont.** LOTUS Analysis Spreadsheet of Manual Cal.

```
LEAST SQUARES FOR SPAN 03
      N        X         Y       N*X       N*Y      YDEV2    est y        X2          Y2          XY rel std dev
-------------------------------------------------------------------------------------------------------------------
      1        8    1.2244         8    1.2244 0.00123716   1.2169        64 1.49915536      9.7952      0.02
      1       29    1.0763        29    1.0763 0.01275243   1.2091       841 1.15842169     31.2127     -0.42
      1       35    1.1207        35    1.1207 0.00469590   1.2069      1225 1.25596849     39.2245     -0.28
      1       41    1.2554        41    1.2554 0.00437891   1.2046      1681 1.57602916     51.4714      0.16
      1       48    1.2427        48    1.2427 0.00285939   1.2020      2304 1.54430329     59.6496      0.13
      1       54    1.2909        54    1.2909   0.008404   1.1998      2916 1.64070481     69.1686      0.26
      0       57        NA         0         0 1.41426006   1.1987         0          0           0        NA
      1       62    1.2772        62    1.2772 0.00773930   1.1968      3844 1.63123984     79.1864      0.26
      1       72    1.2179        72    1.2179 0.00082216   1.1931      5184 1.48328041     87.6888      0.08
      1       97    1.1861        97    1.1861 0.00000977   1.1839      9409 1.40683321    115.0517      0.01
      1      100    1.1883       100    1.1883 0.00000085   1.1827     10000 1.41205689      118.83      0.02
      1      113     1.133       113     1.133 0.00316143   1.1779     12769   1.283689     128.029     -0.14
      1      131    1.1288       131    1.1288 0.00365138   1.1712     17161 1.27418944    147.8728     -0.14
      1      142    1.2246       142    1.2246 0.00125127   1.1671     20164 1.49964516    173.8932      0.18
      1      149    1.1341       149    1.1341 0.00303894   1.1645     22201 1.28618281    168.9809     -0.10
      1      156     1.148       156     1.148 0.00169963   1.1619     24336   1.317904     179.088     -0.04
-------------------------------------------------------------------------------------------------------------------
     15                         1237   17.8384 1.46996265               134099 21.2696035   1459.1428

                      AVE CAL:   1.18922666                SD:       0.31304554 SLOPE:      -3.72E-04
                      XBAR:         82.4667                                     INTER:        1.21989
                                                                                R2:             0.080


********************************************************************************************************

AVE CAL:   Auto Tank 1 : 6/1/85 to 10/17/85

--------   ---------------------------
   NO      response CAL VALUE              decay*
 0.99551    0.59836    0.59568              0.000E+00

response determined from least squares regression, r2, and mean for season


           Auto Cal Gen: 6/1/85 to 10/17/85

           ---------------------------
   03      response CAL VALUE              decay*
 1.18923    0.10094    0.12004              0.000E+00

response determined from least squares regression, r2, and mean for season

decay*    -from least squares regression of response data

CAL VALUE -VALUE ENTERED INTO AUTOCAL DATABASE TO GENERATE DAILY CAL FACTORS
```

**Figure 5, cont.** LOTUS Analysis Spreadsheet of Manual Cal.

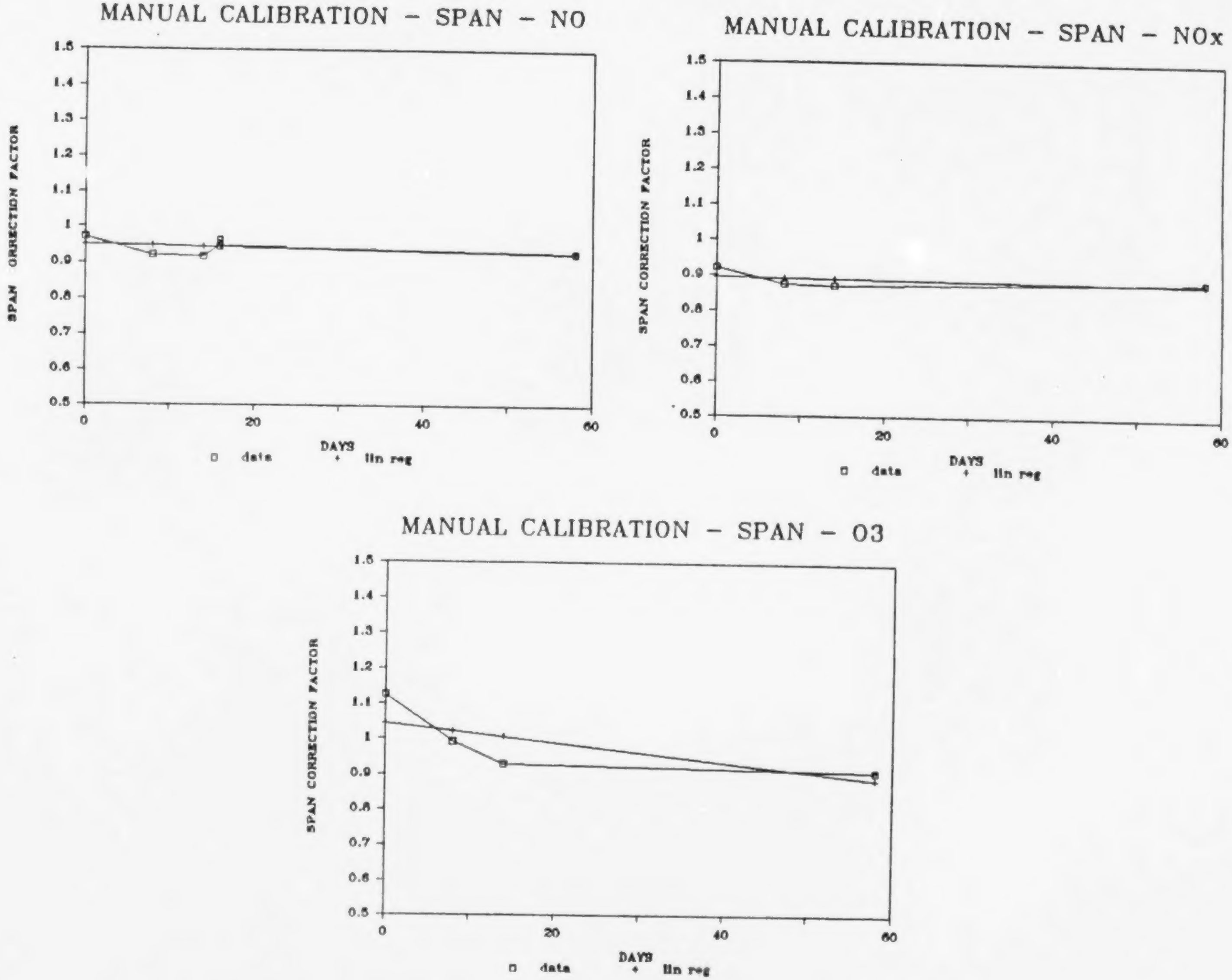


**Figure 6.** LOTUS Analysis Spreadsheet of Manual Cal Plots

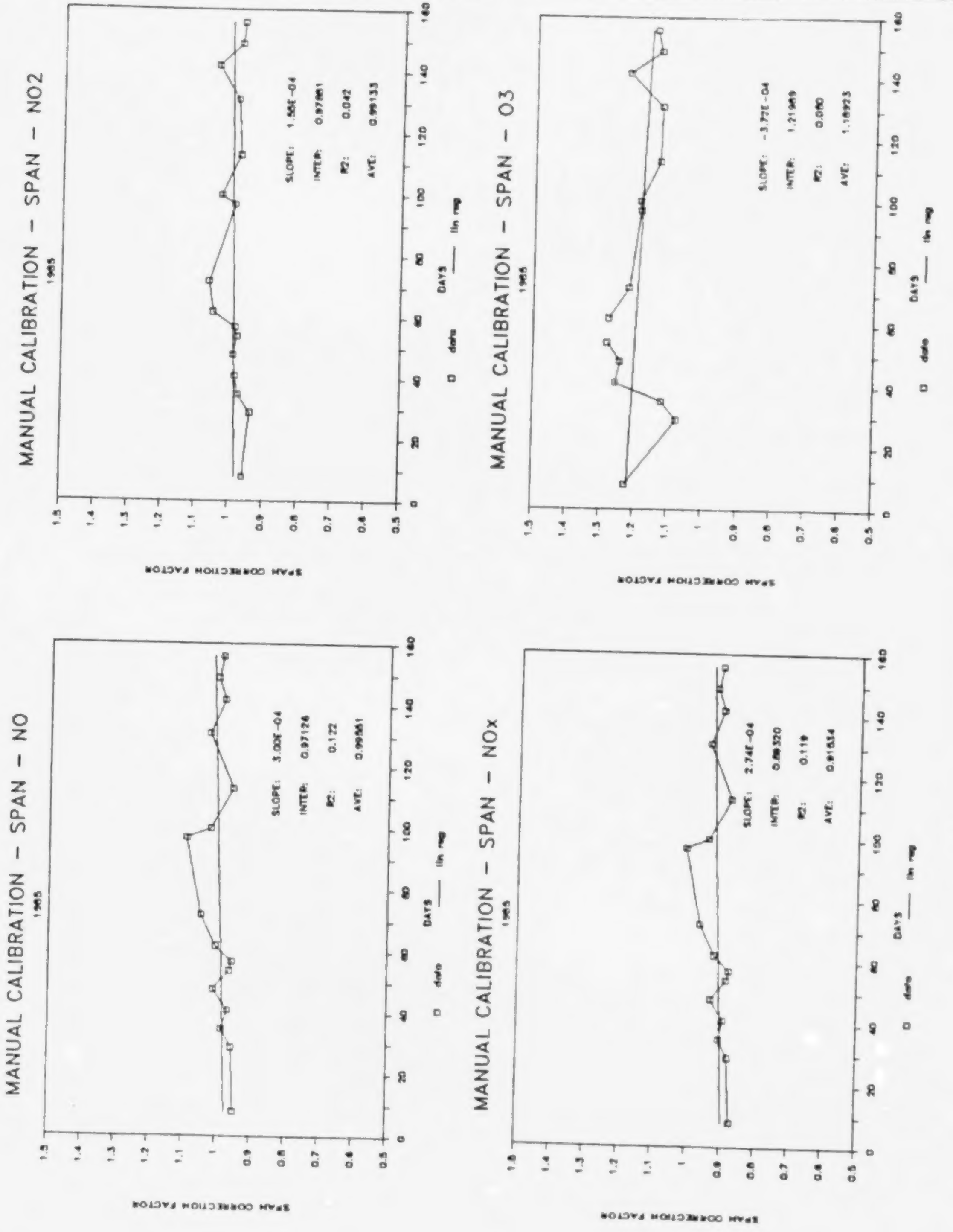


Figure 7. LOTUS Analysis Spreadsheet of Manual Cal Plots

concentration for each species in the tank are listed. The range of agreement is 0.94 to 0.99 with a mean of 0.963 and a relative standard deviation of 1.8 percent; the largest individual relative deviation from the average is 2.5 percent. The agreement between the standard tanks and the RTI tanks is very good. The absolute accuracy of the hydrocarbon calibrations depends directly upon the concentrations assigned to these tanks. In early 1985 we borrowed back the RTI tanks (ethylene and propylene) and another tank containing propane. We compared the calibration factors determined with this tank with calibration factors determined from several other validated sources on two days with three different instruments (see Table 7). The results of the comparison are attached to the end of appendix B. The determined calibration factors for a given instrument with different sources were averaged. The relative standard deviations were calculated. The agreement was very good, with the worst relative standard deviation of 9.2 percent determined for the Carle II gas chromatograph on June 18, 1985. The average relative standard deviation including this value was 3.01 percent. Since the 9.2 value is greater than the average plus two standard deviations, one should consider recomputing the average relative standard deviation without this value: resulting in 1.79 percent.

## Table 7. Intercomparisons Among Sources

| Source | Source | Date |
|---|---|---|
| RTI ethylene | AIRCO | 8/1-2/84 |
| RTI propylene | AIRCO | 8/1-2/84 |
| AIRCO | LOWMW (Hi Conc) | 7/18/84 |
| AIRCO | HIMW (Hi Conc) | 7/18/84 |
| AIRCO | LIQ STD 8/14 | 8/14/84 |
| AIRCO | HIMW (Hi Conc) | 8/14/84 |
| LIQ STD 8/14 (C/area) | HIMW (Hi Conc) | 8/14/84 |
| LIQ STD 8/14 (C/inch) | HIMW (Hi Conc) | 8/14/84 |
| LOWMW (Hi Conc) | LOWMW (Lo Conc) | 7/13/84 |
| LOWMW (Hi Conc) | HIMW (Hi Conc) | 5/30/84 |
| LOWMW (Hi Conc) | 82HCCALMIX | 5/30/84 |
| LOWMW (Hi Conc) | SCOTTTANK | 10/5/84 |
| HIMW (Hi Conc) | SCOTTTANK | 10/5/84 |
| LOWMW (Lo Conc) | SCOTTTANK | 10/5/84 |
| LOWMW (Lo Conc) | SCOTTTANK | 8/17/84 |
| AIRCO | SCOTTTANK | 8/17/84 |
| RTI propane | AIRCO | 6/11/85 |
| RTI propane | LOWMW (Hi Conc) | 6/11/85 |
| RTI propane | RTI propylene | 6/11/85 |
| RTI propane | AIRCO | 6/18/85 |
| RTI propane | LOWMW (Hi Conc) | 6/18/85 |
| RTI propane | RTI propylene | 6/18/85 |

## Table 8. Comparison of Primary HC Calibration Sources

| OCS ID | SOURCE | ANALYZED/ MANUFACTURER avg | std | DEV | REL DEV | ABS REL DEV |
|---|---|---|---|---|---|---|
| 1 | 82HC | 0.971 | 0.126 | 0.008 | 0.8% | 0.8% |
| 108 | HMWHC | 0.985 | 0.047 | 0.022 | 2.3% | 2.3% |
| 109 | LMWHC | 0.956 | 0.034 | -0.007 | -0.7% | 0.7% |
| 112 | AIRCO | 0.939 | 0.101 | -0.024 | -2.5% | 2.5% |
| | ave | 0.963 | 0.077 | | | 1.6% |
| | std | 0.017 | 0.038 | | | 0.8% |
| | rel std | 1.8% | | | | |

## Routine NOx and O3 Calibrations Methods

This section describes the types of calibration methods routinely performed. The section "Calibration Data Processing" describes how the data are processed, including the QA steps. The calibration reports are included or refer to appendices of calibration reports.

### Automatic Source Sampling

The transfer technique to characterize the AUTOCAL sources for $NO_x$ and $O_3$ was described above. Before and after every experiment, these sources plus the AUTOZEROs are used to calibrate the instruments by scheduling 30 minutes to sample from the span sources and from the zero sources by computer control (0200-0230 EDT, 1800-1830 EDT for AUTOZERO; 0230-0300 EDT, 1830-1900 EDT for AUTOSPAN). The two low concentration NO tanks used for AUTOCAL sources are listed in Table 2. The generator built into the $O_3$ monitor is used for the $O_3$ AUTOCAL source.

DATATRIEVE is used to maintain an AUTOCAL database. In this database, the decay rates and the initial concentrations at the beginning of the season are used to estimate the concentration of the span sources for each AUTOCAL performed. A database procedure PRINT_CALS_AND_FACTORS computes calibration factors from the AUTOCAL response and the computed tank concentration.

# Routine HC Calibrations

## Automatic Source Sampling

Routine HC calibrations were performed automatically before every experiment. The GCs are activated several hours before injections and are allowed to produce several chromatograms. A timer switches on the calibration source tank connected to a calibration manifold at approximately 0300 EDT. The flowrate is adjusted to provide an excess which is vented. The timer also switches a three-way valve to change the GCs from the chamber sample manifold to the calibration source manifold. The "low concentration" tank listed in Table 3 and discussed above was the source most commonly used for an AUTOCAL, however other tanks listed in the table were sometimes used. This would normally be when the presence of a morning site operator was required many hours before sunrise. Sometimes calibrations were performed after an experiment when a wider range of calibration species were desired. The site operator indicated on the instrument checklist that a calibration was performed. When the run is logged in later in the data processing office, these notes of calibrations performed will be logged into the calibration database (discussed below).

## Manual Precision Liquid Injections

More extensive calibrations were performed on days that were poor for performing an experiment (poor sun or rain forecast). On these "CAL" days, several tanks would be used for calibrating. More importantly, liquid standards could be injected into the unused chamber for calibrating compounds with vapor pressures too great to be stored in pressurized cylinders (*e.g.*1, 2,4-trimethylbenzene). These calibration data are stored in a "CAL" folder. The presence of the "CAL" folder and a calendar entry indicating a "CAL DAY" will trigger the processing of a calibration that was not performed during an experiment.

Liquid injections of reasonably large amounts (100's of $\mu$l) used to produce initial injections for a smog chamber experiment were usually processed as calibration sources also. The project coordinator decides if the injections are appropriate as a calibration source and then logs in the calibration.

### *Injection Calibration Procedures*

The chamber is usually vented more than 10 hours before injections are made. Hamilton "Standard Microliter " gas chromatography syringes are used to inject known volumes (in 10's to 100's $\mu$l) range) into the smog chamber. Stated accuracy is 1% of the syringe volume. The temperature is recorded for concentration calculations. All data are recorded on the stripchart or by a special note on the `RUN SHEET` or `INSTRUMENT CHECKLIST`.

Injection calibration data are transfered to the Official Calibration Source form (OCS), then to the electronic OCSIC84 form which performs ideal gas law calculations, using the amount injected and the chamber volume. The electronic form automatically looks up density, carbon number, MW *etc.*All calculations are thus recorded. Errors (from improper data transfer or calculation) are therefore minimized.

The determination of chamber volume was by a "strapping" technique. The dimensions of the chamber were carefully measured and used to calculate the volume. Several people have independently made these measurements with less than 1.5% variation in volume.

## Meteorological Sensor Calibrations

### Solar/UV radiation Calibrations

Two sets of both the Eppley Black and White Pyranometer (Total Solar Radiation) and Eppley Ultra-Violet Radiometer (Ultraviolet) sensors are used. One set is used continuously and the other set is reserved as the References. Both sets are calibrated by Eppley. The continuous sensors are sent back to Eppley annually for recalibration. At Epply, the total solar radiation sensor is compared with the Eppley group of reference standards at approximately one half a solar constant. The UV sensor is calibrated by comparison with an Eppley standard of spectral irradiance lamp. More detailed discussion and additional information concerning light measurement is presented in Appendix E.

### Temperature Calibrations

The temperature thermistors are checked against an ice bath and a water bath near normal high afternoon temperature, measured with a general laboratory mercury thermometer.

### Dewpoint Calibrations

There is no direct calibration technique for the dewpoint monitor. The sensor is a high precision point thermometer sensor. The electronics of the instrument must be frequently adjusted to balance the sensor bridge. The detector must also be cleaned routinely. The dewpoint meter is checked by monitoring the saturated air pulled through a water bubbler of known temperature. Response to dry air (air pulled through Drierite) tests for proper cooling circuit operation needed to reach low dewpoints.

## Flowrate Measurements - Calibration

Accurate flowrates are required for the manual gas phase titration method for calibrating $NO_x$ and $O_3$ and for making injections into the smog chamber. The primary standards and routine flowrate measuring devices are a series of 10, 100, 1000, and 2000 milliliter soap bubble flowmeters. The volume of the soap bubble tubes was determined by measuring water volume in NBS calibrated graduated cylinders. A four place digital stopwatch is used for timing.

## Time Measurement - Clock Calibration

All times reported are Eastern Daylight Time, even during winter. The main system clock is housed within the computer. Time is set at the beginning of the run season against standard time reported at the local weather bureau at the Regional Airport. This time is verified several times during the year. Stripcharts are marked at the beginning and throughout the experiment with time read from the computer clock.

## Calibration Documentation and Processing Databases

A formal system has been developed to document and track the processing of the large calibration database. This is important to a QA program to assure that all data is processed and utilized. Various paper and electronic forms, calendars, notebooks, and computer databases are utilized. Forms help assure consistency and completeness. Electronic forms allow for ease of organization, manipulation, retrieval, and analysis. Some of the form fields are actually computed internal to the form.

### Paper Forms

*Run and Calibration Calendars*

Calendars at both the site and the office in the School of Public Health are used to record days on which experiments were conducted. These entries also indicate days on which only calibrations were performed.

*Run Folder Inventory Check Lists*

Instrument Checklists are filled out for each experiment. These lists identify the calibrations that were performed (see Appendix A).

### *Stripcharts*

Stripcharts from an experiment identify the calibrations that were performed, the calibration source, the chart attenuation, the chamber temperature, and the number of microliters that were injected.

### *Manual $NO_x/O_3$ Calibration Form*

Paper forms are used to record manually performed calibrations. These are filled out at the site and transported to the data processing office where they are transfered to electronic form (see below) and stored.

### *Official Calibration Source Form*

All information, including the calibration source concentration used for a calibration, is recorded on Official Calibration Source (OCS) forms (see Figure 8). Information concerned with several stages of processing and several different programs, worksheets, and databases is recorded. The calibration information comes from several sources including stripcharts and attached notes. This form has an id number, identification information, amounts and temperature, and official validated concentration. This information is further stored in a computer database described below which generates a file for processing calibration factors.

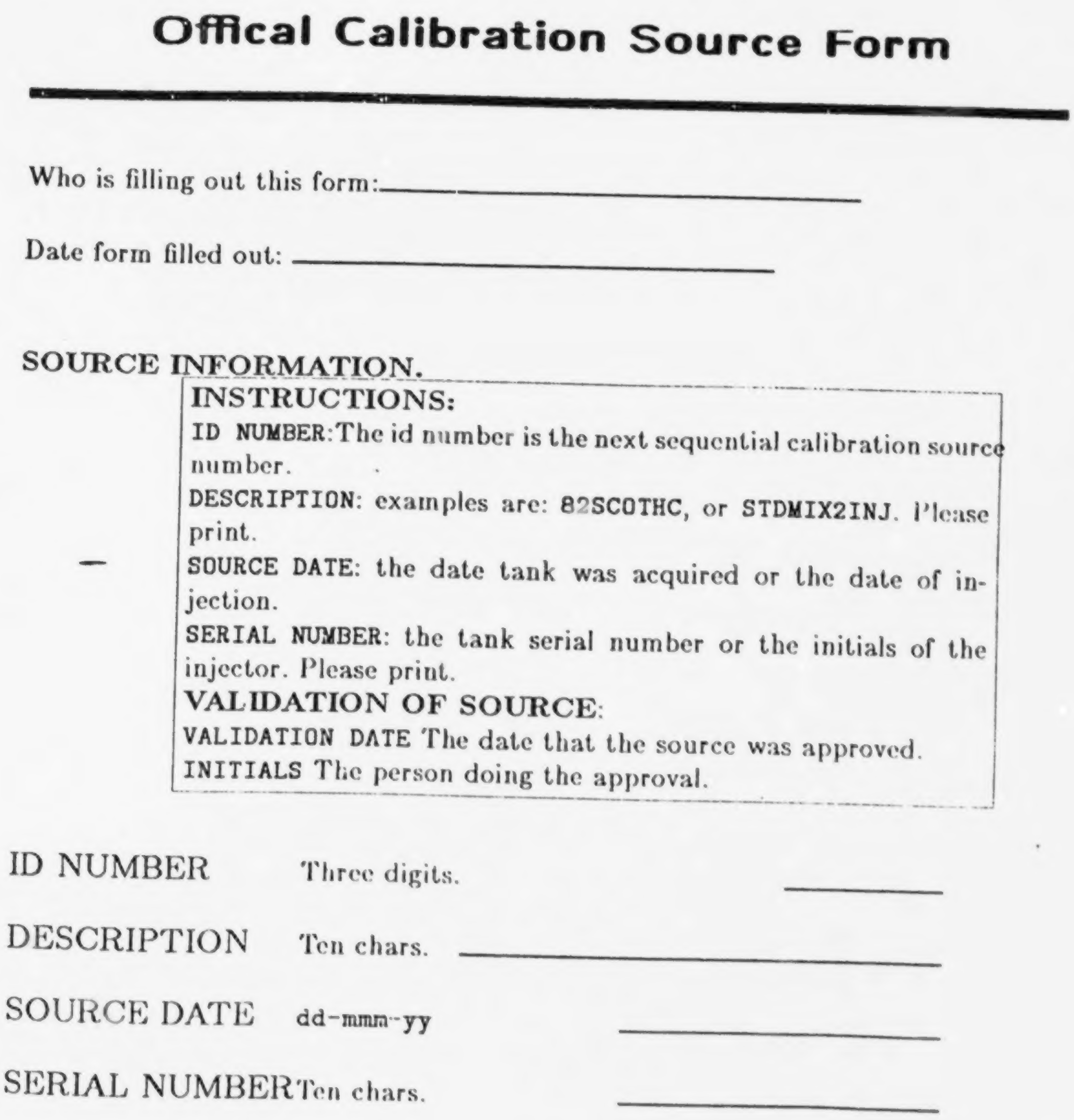
### *Calibration Pick Instructions*

A paper form is used to give and record processing instructions to Data Processors for the raw calibration response data. The location of the calibration data is recorded and the corresponding calibration sources used are identified. Notes can be made about processing status and special problems and processing instructions. Processing status is recorded on this form and concurrently in `CALENTRY`, a computer database for tracking processing status (see below). Figure 9 shows this form.

## Electronic Forms and Other Documentation

### *COMMAND FILE*

Command files are created at the smog chamber site on the computer used to control the experiment. Commands issued to perform auto cals can be used later to document the exact time the instruments are calibrated. Other instruments not directly controlled yet auto calibrated are identified in remarks in the command file.



## Offical Calibration Source Form

Who is filling out this form: ______________________________

Date form filled out: ______________________________

**SOURCE INFORMATION.**

**INSTRUCTIONS:**

`ID NUMBER`:The id number is the next sequential calibration source number.

`DESCRIPTION`: examples are: `82SCOTHC`, or `STDMIX2INJ`. Please print.

`SOURCE DATE`: the date tank was acquired or the date of injection.

`SERIAL NUMBER`: the tank serial number or the initials of the injector. Please print.

**VALIDATION OF SOURCE:**

`VALIDATION DATE` The date that the source was approved.

`INITIALS` The person doing the approval.

ID NUMBER Three digits. __________

DESCRIPTION Ten chars. ______________________________

SOURCE DATE `dd-mmm-yy` ____________________

SERIAL NUMBER Ten chars. ____________________

**Figure 8.** Official Calibration Source Form

**SOURCE VALUE :: one page per species.** Page ________ of ________

SPECIES NAME Full name ____________________

SPECIES NUMBER Three digits ____________

STATED CONC. `9.9999` ____________

ACTUAL CONC. `9.9999` ____________

CONC. UNITS *e.g.* `ppmC` ____________

---

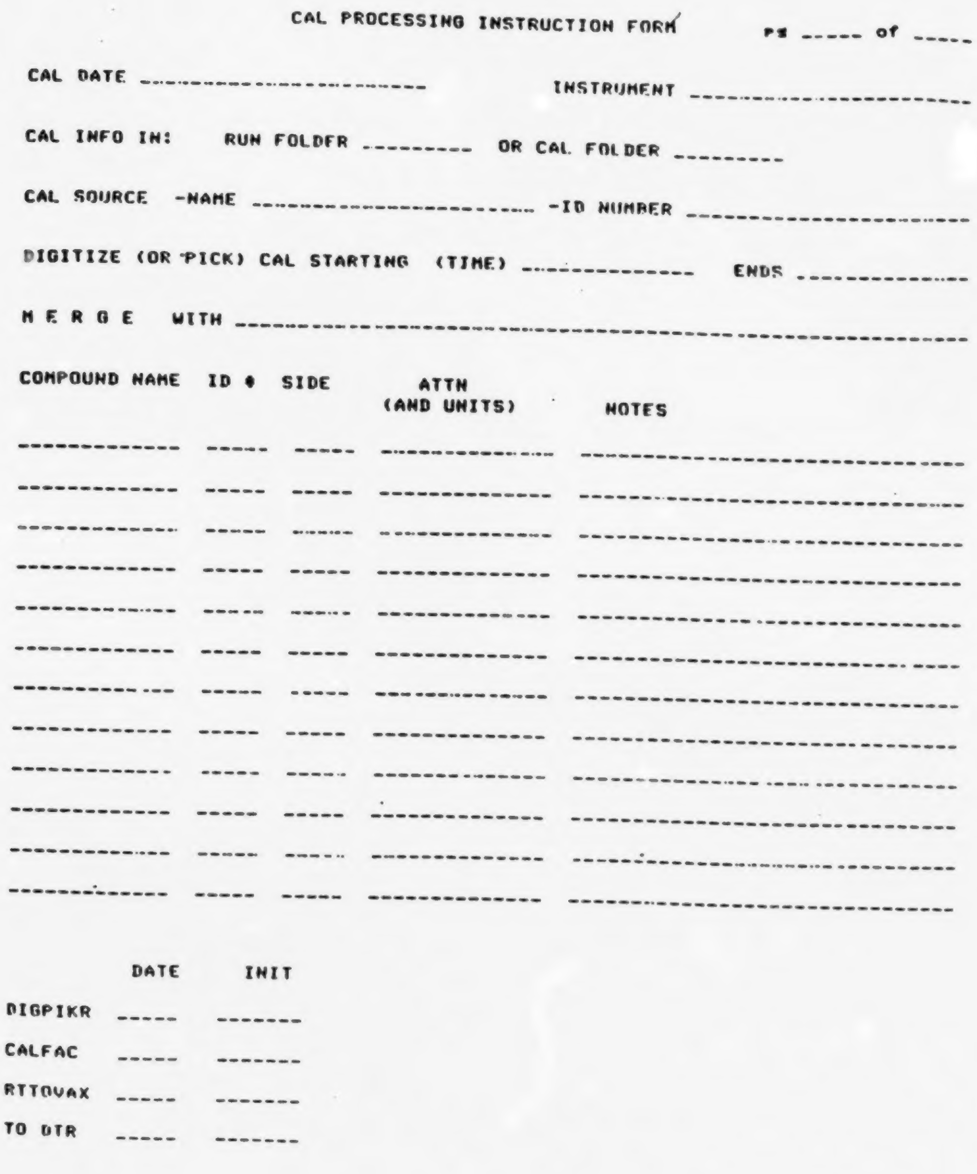
VALIDATION DATE `dd-mmm-yy` ____________

INITIALS ______

---

COMMENTS:

**Figure 8. cont.** Official Calibration Source Form.



CAL PROCESSING INSTRUCTION FORM pg ----- of -----

CAL DATE ------------------------- INSTRUMENT -------------------------

CAL INFO IN: RUN FOLDER --------- OR CAL FOLDER ---------

CAL SOURCE -NAME ------------------------ -ID NUMBER -------------------------

DIGITIZE (OR PICK) CAL STARTING (TIME) --------------- ENDS ---------------

MERGE WITH ----------------------------------------------------------------

| COMPOUND NAME | ID # | SIDE | ATTN (AND UNITS) | NOTES |
|---|---|---|---|---|
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |
| ------------- | ----- | ----- | -------------- | ------------------------------- |

| | DATE | INIT |
|---|---|---|
| DIGPIKR | ----- | ------- |
| CALFAC | ----- | ------- |
| RTTOVAX | ----- | ------- |
| TO DTR | ----- | ------- |

**Figure 9.** Cal Pick Instruction Form

### *REMARKS FILE from Computer DA system*

Another file created during the experiment by the computer is the remarks file which often has comments about calibration events, especially if deviations from the normal procedures are made.

### *Manual $NO_x/O_3$ Calibration Form*

Information from a paper form filled out during a manual $NO_x/O_3$ calibration is manually transferred to electronic form (in LOTUS 123 spreadsheet, see description of general purpose programs below) where the calculations are performed automatically.

### *Official Calibration Source*

A computer database of the Official Calibration Sources also recorded on paper form is maintained on a DEC VAX. This database can be summarized by a database procedure and output in a form used by another program CALFAC to process calibration factors when compared to the response data from a calibration.

### *Injected Conditions as Official Calibration Sources*

Information from paper forms (primarily from the OCS paper form) of injected liquids and solids for calibration is input and processed in electronic form (in LOTUS 123 spreadsheet) where calculations are performed automatically (OCSIC). The spreadsheet looks up the molecular weight, density, and carbon number using the species id number (from the Official Species List), temperature at time of injection, the chamber volume, and the ideal gas law. It was shown earlier as Table 4.

## Calibration Data Processing Status Database (CALENTRY)

A calibration data processing status database called CALENTRY is maintained on the VAX-11/780 using the DATATRIEVE database system. The AA or PC logs in the existence of calibration data for a given instrument and day. The PC and PP update CALENTRY as the various tasks are performed. DATATRIEVE report procedures are used to assist in updating the database, and generating status reports. The PC and PP use the status reports to guide the processing of the calibration data. Table 9 shows the CALENTRY tasks flowchart and the events explained. Table 10 shows an example of the CALSUM report.

## Calibration Databases

Several calibration databases are maintained. Some double as spreadsheets to per-

## Table 9
## Processing System for Instrument Auto-Calibration Data

```
tot inst    cal analysis
      \    /            \
       !CPI!            !OCS!
           \                \
            \                \
             <DPR>----------<CFR>--(Q2V)--(DTR)--(C2L)--<CLR>--!CQA!
```

```
!sss! == stages determined by Project coordinator (PC)
<sss> == stages determined by Peak Pickers (PP)
(sss) == stages determined by Computer Techs (CT)
```

| Step | CALENTRY stages | Meaning |
|---|---|---|
| PC | CPI : CAL pick Inst | Charts marked, cal status sheet in folder |
| PP | DPR : Digpik run | Cal data digitized and R-file exists |
| PC | OCS : OCS ok | Official Cal Source exists in DTR |
| PP | CFR : CALFAC run | Cal Factor computed, Q-file created |
| CT | Q2V : Qfile to vax | Q-file moved to VAX |
| CT | DTR : DTR file updated | Cal Data added to DTR data base |
| CT | C2L : Cals to LSI | DTR CAL file loaded on LSI-11 |
| PP | CLR : CALANA run | Cal Factors analyzed |
| PC | CQA : Cal QA | Cal Factor Quality Assurance |
| PC | NTB : Not to be proc | Not to be processed |
| PC | BAD : Stop processing | Something is wrong with this run |

Table 10. CALSUM Example

```
Count of calibrations that have reached stated stages of processing
          for METH

Total calibrations

       265

######## HC Instrument data #############

CPI DPR OCS CFR Q2V DTR C2L CLR CQA C2S NTB BAD

181 181 181 181 179 179   0   0 144   0  53   9

     Sum of CPI and NTB is  234
```

```
                    CAL PROCESSING STATUS                  6-May-1985
                                                           Page 5

    CAL
    DATE  Instrument                        Calibration
                                               Steps
     Carle III GC                       CAL pick Inst
                                        Digpik run
                                        CALFAC run
13-Jul-1984
     Carle I   GC                       CAL pick Inst
                                        Digpik run
                                        CALFAC run
     Carle II  GC                       CAL pick Inst
                                        Digpik run
                                        CALFAC run
     Carle III GC                       CAL pick Inst
                                        Digpik run
                                        CALFAC run
     CEA Formaldehyde                   CAL pick Inst
                                        Digpik run
                                        CALFAC run
14-Jul-1984
     Carle I   GC                       CAL pick Inst
                                        Digpik run
                                        CALFAC run
     Carle II  GC                       CAL pick Inst
                                        Digpik run
                                        CALFAC run
     Carle III GC                       CAL pick Inst
                                        Digpik run
                                        CALFAC run
16-Jul-1984
     Carle I   GC                       CAL pick Inst
                                        Digpik run
                                        CALFAC run
     Carle II  GC                       CAL pick Inst
                                        Digpik run
                                        CALFAC run
     Carle III GC                       Not to be proc
```

form calculations. The databases serve several functions. Database commands and procedures can sort by instrument and species, make plots of cal-factors vs time, perform regression and correlation calculations, convert to a common attenuation or range, output reports, output files for other programs, and in general allow us to organize, retrieve and update information easily.

### *HC Tank Calibration Source Certification Database ("CAL")*

Many different calibration sources were used for hydrocarbons. Some are "cal" tanks and others are analyzed by the manufacturer with a stated uncertainty. Liquids injected into the chamber are another calibration source. All "cal" sources were intercompared to check for consistency. Data was collected in both peak height and integrator area, and organized in a LOTUS 123 spreadsheet database. Calculations of the intercomparison were then performed (see Appendix B).

### *Official Calibration Sources (OCS) Database*

The Official Calibration Sources (OCS) Database were mentioned earlier in the electronic forms section. The database utilizes DATATRIEVE on the VAX-11/780. The database appears as a collection of forms on terminal screens which makes updating easier. Procedures have been written to generate reports (see Appendix C) and a file of the calibration source data required by the program CALFAC used to calculate the calibration factors.

### *Gas Phase Titration Database ("MANCAL" LOTUS 123 )*

The resulting calculations (calibration correction factors) processed from the raw calibration zero and response data are summarized and analyzed in another database/spreadsheet using LOTUS 123. Plots of calibration data vs time with regressions and correlation are produced easily. Trends and variation are easily recognized. Reports are quickly produced.

### $NO_x$ *and* $O_3$ *Auto-calibration Database: AUTOCAL*

The $NO_x$ and $O_3$ AUTOCAL data are maintained in a separate DATATRIEVE database. Instrument calibration zeros and responses to the AUTOCAL sources are recorded. Report procedures compare the corrected responses to the known calibration source concentration and generate and list the calibration factors, sorted by date and time of day (autocals for $NO_x$ and $O_3$ are usually performed twice a day).

### *Hydrocarbon Auto-Calibration Database*

Another DATATRIEVE database similar to the $NO_x$ and $O_3$ AUTOCAL database is maintained for hydrocarbon calibration data. The database is more complex because of the many more instruments which are calibrated. The database is also much larger. A calibration factor is recorded for each species. Attenuation is also recorded. Interactive report procedures can retrieve and sort calibration data by instrument, species, and date, and convert calibration data to a common attenuation. This report is the primary source of final calibration data used to process data. Another procedure outputs a file which can be read by another custom program (CALANA) which statistically analyzes calibration data for a given species instrument combination and plots the calibration history for the run season.

### *Calibration Factors Used Database*

Another DATATRIEVE database is used to record the calibration factors actually used to process the final experimental time-concentration data. Some interpretation and choice must be made when the statistics and the various sources of calibration factors do not agree. The PC makes a judgement based on all calibration information and chooses a calibration factor. The chosen calibration factor is kept in a separate data base. The resulting calibration factor database is maintained as a final source of information for making a choice in a calibration factor. We believe that except for rare occurences, calibration factors for most instruments do not vary much. This database is consulted to see if the calibration factor chosen varies much from those used on data from days (experiments) before and after the current experiment being processed.

## Security of Calibration Databases

There are three basic approaches to data security: inventory, retention of original data in restricted areas, and maintaining several backup copies of all data in different locations. All data are under lock at night and on weekends.

### *Inventory*

At the site during an experiment, the calibrations that were performed are indicated on a Instrument Checklist Form. Afterwards, before anyone is allowed to work with the run folder contents, a run folder inventory is performed which documents all data and forms. This assures that no data or documentation are lost.

### *Retention of Data*

All original data in both paper and electronic files are retained. Paper format data (all stripcharts, forms) are not allowed out of the School of Public Health office.

### *Backup of Data*

Multiple copies of data are maintained in several formats, in several locations. Backup copies of raw and final data on floppies on IBM PC are kept in several locations. LOTUS 123 worksheet files are backed up in two locations. A hardcopy (printout) of worksheet formulas using a spreadsheet AUDITOR program is kept. Backup copies of raw and final data on LSI-11 computers are maintained in several locations, including: raw data and processed data sets backed up on two diskettes, processing programs (sources) backed up on two diskettes, and whole image backup of LSI hard disk. Backup copies of final data are maintained on the VAX and are further backed-up on tapes of VAX files. There are also frequent printouts of final calibration data in notebooks. The school operates a daily, weekly, and monthly backup of VAX files with off-site vault storage for ten years for all VAX data.

## Calibration Data Processing

This section describes and illustrates the actual data processing procedures. Processing techniques are discussed separately for $NO_x/O_3$ and HC data, because of the different data and processing requirements and the different type of calibration sources. The databases are also maintained separately. Another important distinction is the way the different types of calibration data are transported from the smog chamber to the data processing office in the School of Public Health.

### $NO_x$ and $O_3$

#### *Manual Calibration Processing for Characterization of* AUTOCAL *Sources*

The calibration sources used for the $NO_x$ and $O_3$ monitors were discussed above. Also discussed was the relationship between the manual and auto calibrations performed. The manually performed gas phase titration calibrations are used to calibrate the auto calibration sources.

#### AUTOCAL *Data Processing*

AUTOCAL data for zeros and spans is obtained twice daily. The PDP/11-40 computer at the site initiates the calibration from a COMMAND file written by a site operator (30 minutes zero; 30 minutes span). The calibration data is recorded along with the experimental results by the computer DA system (one value every minute). Therefore the calibration data is transported along with the electronic data. Figure 10 shows a flowchart of the autocalibration data processing procedures. These tasks are mostly performed by the CT.

A computer program was written (FASTDV) to strip the calibration data from the DVM data file (see Figure 10). One file is made for every AUTOCAL performed. There are usually two autocals per day. The files are named MMDDYA.DVn where n is 1st and 2nd calibration performed. These are called "A-files". The files are backed-up on floppies. Each file is edited if necessary to eliminate readings taken in transition to the calibration value. These edited files are named MMDDYE.DVn ("E files"). These are also backed-up on floppies. They are then appended together into a file called AUTCAL.NEW. This file is appended to AUTCAL.DVM which is the "OFFICIAL" file of appended "E files", which is also backed-up on floppies.

The AUTCAL.NEW file is further processed. It is averaged to a single value for both zero and span with the program called ACALAV on the LSI-11/23. A listing of the processed averaged data is made and stored in the $NO_x/O_3$ FASTPLOT notebook. This program generates a file called ACDTR.COM which contains the processed averaged calibration data with additional DATATRIEVE commands. The file is transferred to the VAX and activated as a command procedure which causes the data to be automatically entered into the DATATRIEVE AUTOCAL database. The database also contains the characterized concentration values of the AUTOCAL sources (see discussion above). A report procedure in DATATRIEVE called PRINT_CALS_AND_FACTORS reports the original calibration data by date and time and reports the calculated correction factors. In 1985, a somewhat different procedure was utilized. Autocal data were digitized from the stripcharts of the NOx and O3 instruments. "P"-files of the autocal data were imported into a Lotus 123 database-spreadsheet file for processing. The database software on the VAX was not used. Otherwise the processing techniques were the same in 1984 and 1985. Table 11 and Table 12 show the final AUTOCAL calibration factors for 1984 and 1985.

## HC Processing

Processing of hydrocarbon calibration data is more complicated than processing $NO_x$ and $O_3$ calibration data. Each gas chromatograph monitors dozens, potentially hundreds, of different compounds. Each species used in an experiment requires a calibration factor for each instrument. Not every species is calibrated explicitly before every experiment. Several different calibration sources are used. Resulting calibration data must be reviewed before assigning a value for final data processing. An explicit calibration source for a compound monitored in an experiment may not exist and other techniques must be used to establish an appropriate calibration

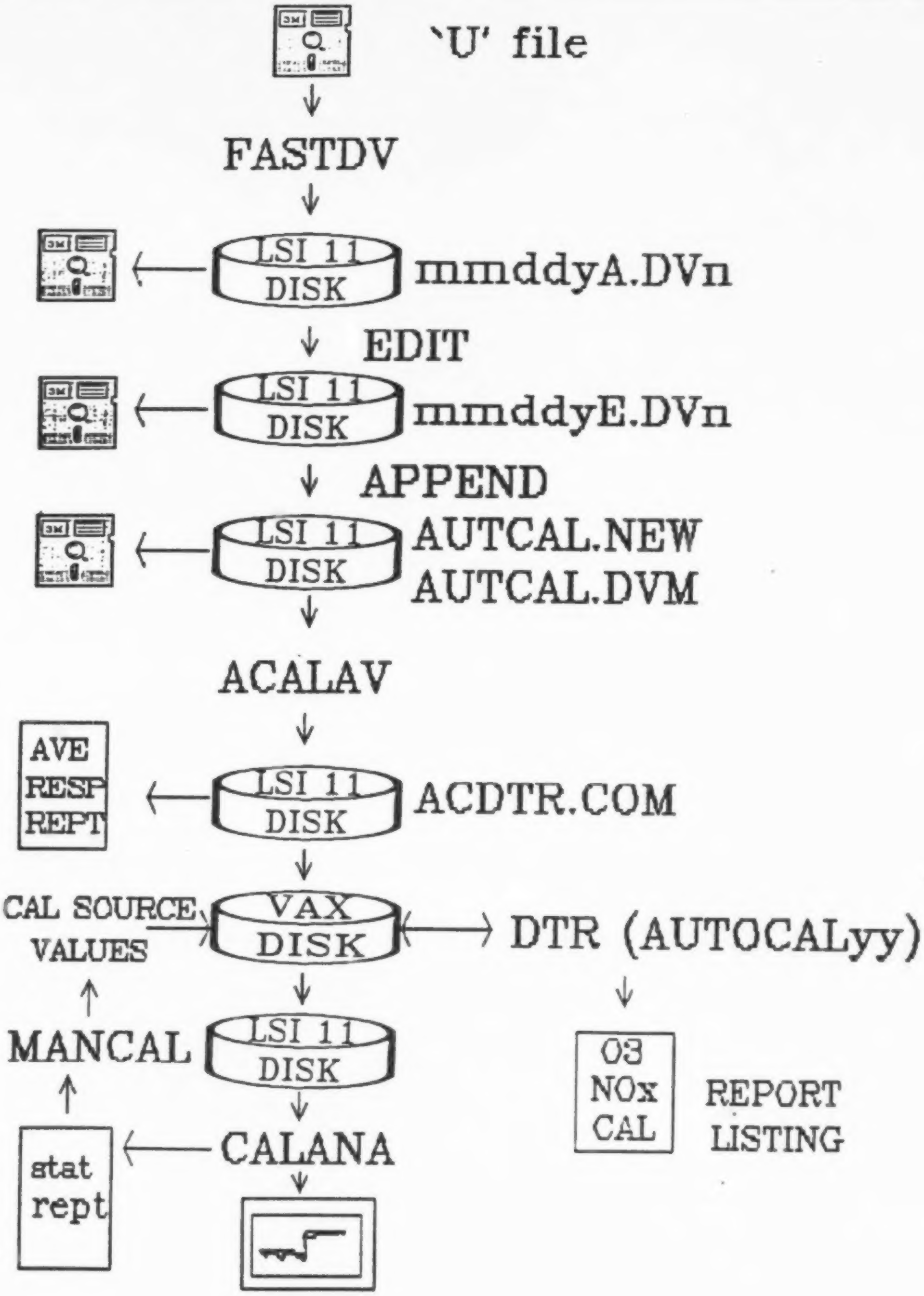

'U' file
FASTDV
LSI 11 DISK
mmddyA.DVn
EDIT
LSI 11 DISK
mmddyE.DVn
APPEND
LSI 11 DISK
AUTCAL.NEW
AUTCAL.DVM
ACALAV
AVE RESP REPT
LSI 11 DISK
ACDTR.COM
CAL SOURCE VALUES
VAX DISK
DTR (AUTOCALyy)
MANCAL
LSI 11 DISK
O3 NOx CAL
REPORT LISTING
stat rept
CALANA

Figure 10. AUTOCAL Processing Flowchart.

## Table 11. NOX AND O3 CALIBRATIONS FOR 1984

16-May-1985

| DATE | NOX ZERO | NO ZERO | NO2 ZERO | O3 ZERO | NOX SPAN | NO SPAN | O3 SPAN | NOX RESP | NO RESP | O3 RESP | NO CAL | NOX CAL | O3 CAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Jun23 | -0.0026 | 0.0001 | -0.0015 | -0.0140 | 0.3259 | 0.3101 | 0.1139 | 0.3295 | 0.3100 | 0.1287 | 0.9268 | 0.8746 | 0.9235 |
| Jun25 | -0.0026 | -0.0004 | -0.0010 | 0.0000 | -9.9999 | -9.9999 | -9.9999 | -9.9973 | -9.9995 | ******** | -0.0207 | -0.0207 | -0.0119 |
| Jun25 | -0.0026 | -0.0006 | -0.0004 | 0.0011 | 0.3208 | 0.3061 | 0.1253 | 0.3226 | 0.3067 | 0.1242 | 0.9364 | 0.8903 | 0.9550 |
| Jun26 | 0.0012 | 0.0025 | -0.0004 | 0.0000 | 0.3267 | 0.3116 | 0.1234 | 0.3255 | 0.3091 | 0.1276 | 0.9290 | 0.8822 | 0.9290 |
| Jun26 | -0.0014 | -0.0008 | 0.0004 | 0.0022 | 0.3190 | 0.3062 | 0.1273 | 0.3204 | 0.3070 | 0.1251 | 0.9354 | 0.8962 | 0.9404 |
| Jun27 | -0.0013 | 0.0005 | -0.0006 | 0.0007 | 0.3256 | 0.3121 | 0.1290 | 0.3269 | 0.3116 | 0.1283 | 0.9214 | 0.8783 | 0.9242 |
| Jun27 | -0.0025 | -0.0009 | -0.0004 | 0.0012 | 0.3207 | 0.3059 | 0.1261 | 0.3232 | 0.3070 | 0.1249 | 0.9320 | 0.8883 | 0.9493 |
| Jun28 | -0.0020 | 0.0000 | -0.0010 | 0.0007 | 0.3248 | 0.3090 | 0.1275 | 0.3260 | 0.3090 | 0.1260 | 0.9266 | 0.8704 | 0.9345 |
| Jun29 | -0.0019 | -0.0006 | 0.0002 | 0.0019 | -9.9999 | -9.9999 | 0.1204 | -9.9980 | -9.9993 | 0.1265 | -0.0207 | -0.0207 | 0.9367 |
| Jul06 | -0.0002 | 0.0000 | 0.0003 | 0.0002 | 0.3140 | 0.2980 | 0.1228 | 0.3150 | 0.2980 | 0.1226 | 0.9620 | 0.9100 | 0.9619 |
| Jul07 | -0.0014 | 0.0010 | -0.0012 | 0.0007 | 0.3130 | 0.2985 | 0.1263 | 0.3152 | 0.2975 | 0.1256 | 0.9634 | 0.9093 | 0.9303 |
| Jul07 | -0.0012 | 0.0008 | -0.0001 | 0.0010 | 0.3105 | 0.2954 | 0.1225 | 0.3117 | 0.2954 | 0.1215 | 0.9703 | 0.9195 | 0.9700 |
| Jul09 | -0.0009 | 0.0013 | -0.0005 | 0.0007 | 0.3193 | 0.3039 | 0.1264 | 0.3202 | 0.3026 | 0.1257 | 0.9469 | 0.8940 | 0.9364 |
| Jul09 | -0.0025 | 0.0002 | -0.0011 | 0.0009 | 0.3130 | 0.2988 | 0.1255 | 0.3155 | 0.2986 | 0.1246 | 0.9595 | 0.9001 | 0.9447 |
| Jul10 | -0.0013 | 0.0010 | -0.0007 | 0.0006 | 0.3163 | 0.3016 | 0.1264 | 0.3176 | 0.3006 | 0.1250 | 0.9530 | 0.9020 | 0.9351 |
| Jul10 | -0.0021 | 0.0004 | -0.0007 | 0.0011 | 0.3119 | 0.2974 | 0.1146 | 0.3140 | 0.2970 | 0.1135 | 0.9645 | 0.9123 | 1.0364 |
| Jul11 | -0.0016 | 0.0008 | -0.0000 | 0.0006 | 0.3145 | 0.2994 | 0.1140 | 0.3161 | 0.2906 | 0.1142 | 0.9592 | 0.9061 | 1.0295 |
| Jul11 | -0.0026 | -0.0003 | -0.0005 | 0.0010 | 0.3060 | 0.2920 | 0.1116 | 0.3006 | 0.2931 | 0.1106 | 0.9772 | 0.9281 | 1.0630 |
| Jul20 | -0.0011 | 0.0007 | 0.0002 | 0.0007 | 0.3205 | 0.3061 | 0.1111 | 0.3216 | 0.3054 | 0.1104 | 0.9364 | 0.8892 | 1.0590 |
| Jul21 | -0.0003 | 0.0010 | 0.0005 | 0.0096 | 0.3224 | 0.3077 | 0.1142 | 0.3227 | 0.3067 | 0.1136 | 0.9323 | 0.8861 | 1.0286 |
| Jul21 | -0.0006 | 0.0028 | 0.0009 | 0.0010 | 0.3208 | 0.3061 | 0.1146 | 0.3214 | 0.3053 | 0.1136 | 0.9366 | 0.8896 | 1.0266 |
| Jul22 | -0.0007 | 0.0013 | 0.0005 | 0.0000 | 0.3229 | 0.3071 | 0.1175 | 0.3236 | 0.3050 | 0.1167 | 0.9349 | 0.8834 | 1.0006 |
| Jul22 | -0.0009 | 0.0004 | 0.0006 | 0.0012 | -9.9999 | -9.9999 | 0.1174 | -9.9990 | ******** | 0.1162 | -0.0286 | -0.0286 | 1.0049 |
| Jul24 | -0.0004 | 0.0013 | 0.0006 | 0.0007 | 0.3220 | 0.3071 | 0.1204 | 0.3224 | 0.3050 | 0.1197 | 0.9345 | 0.8864 | 0.9744 |
| Jul24 | -0.0033 | -0.0009 | 0.0003 | 0.0007 | 0.3130 | 0.2987 | 0.1155 | 0.3163 | 0.2996 | 0.1148 | 0.9539 | 0.9035 | 1.0160 |
| Jul25 | -0.0008 | 0.0009 | 0.0002 | 0.0006 | 0.3200 | 0.3053 | 0.1106 | 0.3200 | 0.3044 | 0.1100 | 0.9387 | 0.8907 | 0.9870 |
| Jul25 | -0.0019 | 0.0031 | 0.0005 | 0.0009 | -9.9999 | -9.9999 | 0.1160 | -9.9970 | ******** | 0.1151 | -0.0286 | -0.0286 | 1.0127 |
| Jul26 | -0.0010 | 0.0008 | 0.0005 | 0.0007 | -9.9999 | -9.9999 | 0.1180 | -9.9989 | ******** | 0.1101 | -0.0286 | -0.0286 | 0.9863 |
| Jul26 | -0.0016 | 0.0002 | 0.0005 | 0.0016 | 0.3100 | 0.3030 | 0.1173 | 0.3196 | 0.3020 | 0.1157 | 0.9435 | 0.8939 | 1.0060 |
| Jul28 | 0.0010 | 0.0012 | 0.0018 | -0.0021 | 0.3219 | 0.3066 | 0.1168 | 0.3209 | 0.3054 | 0.1189 | 0.9351 | 0.8900 | 0.9705 |
| Jul28 | 0.0023 | 0.0012 | 0.0034 | -0.0008 | 0.3237 | 0.3079 | 0.1163 | 0.3214 | 0.3067 | 0.1171 | 0.9312 | 0.8886 | 0.9935 |
| Jul29 | 0.0000 | 0.0017 | 0.0005 | -0.0011 | 0.3239 | 0.3094 | 0.1189 | 0.3239 | 0.3077 | 0.1200 | 0.9280 | 0.8816 | 0.9609 |
| Jul29 | -0.0003 | 0.0013 | 0.0060 | -0.0014 | 0.3244 | 0.3093 | 0.1103 | 0.3247 | 0.3000 | 0.1197 | 0.9271 | 0.8794 | 0.9714 |
| Jul31 | 0.0001 | 0.0018 | 0.0016 | 0.0006 | 0.3193 | 0.3010 | 0.1210 | 0.3192 | 0.3032 | 0.1212 | 0.9414 | 0.8942 | 0.9592 |
| Aug02 | -0.0030 | -0.0005 | 0.0009 | 0.0006 | 0.3424 | 0.3164 | 0.1212 | 0.3454 | 0.3169 | 0.1206 | 0.9064 | 0.8261 | 0.9617 |
| Aug02 | -0.0021 | -0.0010 | 0.0008 | 0.0013 | 0.3342 | 0.3155 | 0.1200 | 0.3363 | 0.3165 | 0.1107 | 0.9016 | 0.8485 | 0.9771 |
| Aug03 | -0.0018 | 0.0002 | 0.0004 | 0.0007 | 0.3249 | 0.3002 | 0.1210 | 0.3267 | 0.3000 | 0.1211 | 0.9263 | 0.8733 | 0.9572 |
| Aug03 | -0.0030 | -0.0009 | 0.0004 | 0.0009 | 0.3163 | 0.3014 | 0.1107 | 0.3193 | 0.3023 | 0.1178 | 0.9437 | 0.8935 | 0.9040 |
| Aug04 | -0.0042 | -0.0020 | 0.0002 | 0.0007 | 0.3150 | 0.2999 | 0.1161 | 0.3200 | 0.3019 | 0.1154 | 0.9440 | 0.8914 | 1.0030 |
| Aug04 | -0.0032 | -0.0069 | 0.0003 | 0.0008 | -9.9999 | -9.9999 | 0.1172 | -9.9967 | -9.9990 | 0.1164 | -0.0285 | -0.0285 | 0.9952 |
| Aug05 | -0.0039 | -0.0023 | 0.0000 | 0.0008 | -9.9999 | -9.9999 | 0.1126 | -9.9960 | -9.9976 | 0.1118 | -0.0285 | -0.0285 | 1.0255 |
| Aug05 | -0.0034 | -0.0012 | 0.0005 | 0.0009 | 0.3153 | 0.3012 | 0.1144 | 0.3187 | 0.3024 | 0.1135 | 0.9431 | 0.8949 | 1.0240 |
| Aug06 | -0.0042 | -0.0021 | 0.0007 | 0.0007 | 0.3141 | 0.2931 | 0.1096 | 0.3103 | 0.3012 | 0.1089 | 0.9467 | 0.8950 | 1.0624 |
| Aug06 | -0.0040 | -0.0020 | 0.0004 | 0.0000 | 0.3122 | 0.2982 | 0.1162 | 0.3162 | 0.3002 | 0.1154 | 0.9499 | 0.9010 | 1.0026 |
| Aug07 | -0.0057 | -0.0031 | 0.0006 | 0.0007 | 0.3101 | 0.2960 | 0.1140 | 0.3150 | 0.2991 | 0.1141 | 0.9532 | 0.9020 | 1.0134 |
| Aug07 | -0.0034 | -0.0018 | 0.0004 | 0.0015 | 0.3111 | 0.2975 | 0.1172 | 0.3145 | 0.2993 | 0.1157 | 0.9525 | 0.9065 | 0.9994 |
| Aug08 | -0.0062 | -0.0036 | 0.0004 | 0.0007 | 0.3006 | 0.2950 | 0.1164 | 0.3140 | 0.2986 | 0.1157 | 0.9546 | 0.9055 | 0.9907 |
| Aug08 | -0.0030 | -0.0021 | 0.0003 | 0.0000 | 0.3111 | 0.2973 | 0.1181 | 0.3149 | 0.2994 | 0.1173 | 0.9521 | 0.9052 | 0.9851 |
| Aug16 | -0.0000 | 0.0001 | 0.0015 | 0.0006 | 0.3230 | 0.3071 | 0.1203 | 0.3230 | 0.3070 | 0.1197 | 0.9272 | 0.8791 | 0.9606 |

## Table 11, cont. NOX AND O3 CALIBRATIONS FOR 1984

16-May-1985

| DATE | NOX ZERO | NO ZERO | NO2 ZERO | O3 ZERO | NOX SPAN | NO SPAN | O3 SPAN | NOX RESP | NO RESP | O3 RESP | NO CAL | NOX CAL | O3 CAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aug10 | -0.0040 | -0.0027 | 0.0011 | 0.0007 | 0.3164 | 0.3019 | 0.1167 | 0.3204 | 0.3046 | 0.1160 | 0.9342 | 0.8881 | 0.9900 |
| Aug18 | -0.0045 | -0.0025 | 0.0004 | 0.0007 | 0.3172 | 0.2999 | 0.1162 | 0.3217 | 0.3024 | 0.1155 | 0.9410 | 0.0045 | 0.9943 |
| Aug19 | -0.0047 | -0.0027 | 0.0032 | 0.0008 | 0.3140 | 0.2999 | 0.1175 | 0.3187 | 0.3026 | 0.1167 | 0.9402 | 0.8927 | 0.9824 |
| Aug19 | -0.0035 | -0.0020 | 0.0009 | 0.0015 | 0.3139 | 0.2906 | 0.1183 | 0.3174 | 0.3006 | 0.1160 | 0.9465 | 0.8964 | 0.9826 |
| Aug20 | -0.0048 | -0.0027 | 0.0006 | 0.0008 | 0.3140 | 0.3002 | 0.1192 | 0.3196 | 0.3029 | 0.1104 | 0.9391 | 0.8901 | 0.9567 |
| Aug20 | -0.0047 | -0.0031 | 0.0010 | 0.0010 | 0.3147 | 0.3004 | 0.1165 | 0.3194 | 0.3035 | 0.1175 | 0.9373 | 0.8906 | 0.9701 |
| Aug22 | -0.0045 | -0.0034 | 0.0014 | 0.0008 | 0.3183 | 0.3037 | 0.1200 | 0.3220 | 0.3071 | 0.1200 | 0.9260 | 0.8809 | 0.9546 |
| Aug22 | -0.0012 | -0.0023 | 0.0030 | 0.0008 | 0.3209 | 0.3049 | 0.1201 | 0.3221 | 0.3072 | 0.1193 | 0.9257 | 0.8828 | 0.9602 |
| Aug23 | -0.0036 | -0.0026 | 0.0016 | 0.0008 | 0.3197 | 0.3044 | 0.1265 | 0.3233 | 0.3070 | 0.1257 | 0.9261 | 0.8794 | 0.9187 |
| Aug25 | 0.0050 | 0.0000 | 0.0060 | 0.0010 | 0.3140 | 0.2945 | 0.1215 | 0.3090 | 0.2945 | 0.1205 | 0.9651 | 0.9193 | 0.9460 |
| Aug25 | 0.0020 | -0.0010 | 0.0050 | 0.0010 | 0.3155 | 0.2965 | 0.1250 | 0.3135 | 0.2975 | 0.1240 | 0.9553 | 0.9066 | 0.9220 |
| Aug27 | 0.0016 | -0.0014 | 0.0044 | 0.0023 | 0.3165 | 0.2992 | 0.1255 | 0.3149 | 0.3006 | 0.1232 | 0.9452 | 0.9022 | 0.9269 |
| Aug28 | -0.0010 | -0.0018 | 0.0031 | 0.0008 | 0.3144 | 0.2983 | 0.1246 | 0.3154 | 0.3001 | 0.1240 | 0.9466 | 0.9007 | 0.9203 |
| Aug29 | -0.0022 | -0.0026 | 0.0026 | 0.0008 | 0.3143 | 0.2980 | 0.1246 | 0.3165 | 0.3006 | 0.1238 | 0.9440 | 0.8974 | 0.9212 |
| Aug29 | -0.0007 | -0.0018 | 0.0027 | 0.0008 | 0.3129 | 0.2972 | 0.1185 | 0.3136 | 0.2990 | 0.1177 | 0.9499 | 0.9057 | 0.9698 |
| Sep01 | -0.0014 | -0.0022 | 0.0031 | 0.0017 | 0.3153 | 0.2997 | 0.1172 | 0.3167 | 0.3019 | 0.1155 | 0.9403 | 0.8963 | 0.9856 |
| Sep01 | -0.0014 | -0.0022 | 0.0031 | 0.0017 | 0.7439 | 0.7060 | 0.1172 | 0.7453 | 0.7082 | 0.1155 | 0.9389 | 0.8957 | 0.9856 |
| Sep02 | -0.0028 | -0.0028 | 0.0028 | 0.0008 | 0.7377 | 0.6920 | 0.1172 | 0.7405 | 0.6940 | 0.1164 | 0.9563 | 0.9009 | 0.9773 |
| Sep02 | -0.0037 | -0.0031 | 0.0018 | 0.0007 | 0.7377 | 0.6920 | 0.1172 | 0.7414 | 0.6951 | 0.1165 | 0.9559 | 0.8998 | 0.9765 |
| Sep02 | -0.0027 | -0.0025 | 0.0019 | 0.0007 | 0.7269 | 0.6813 | 0.1199 | 0.7296 | 0.6838 | 0.1182 | 0.9717 | 0.9144 | 0.9624 |
| Sep03 | -0.0042 | -0.0021 | -0.0001 | 0.0009 | 0.7390 | 0.6949 | 0.1173 | 0.7432 | 0.6970 | 0.1164 | 0.9526 | 0.8970 | 0.9767 |
| Sep06 | 0.0055 | 0.0003 | 0.0073 | 0.0008 | 0.7447 | 0.6969 | 0.1193 | 0.7392 | 0.6966 | 0.1185 | 0.9511 | 0.9000 | 0.9576 |
| Sep06 | 0.0061 | 0.0017 | -9.9999 | 0.0022 | 0.7447 | 0.6969 | 0.1195 | 0.7306 | 0.6952 | 0.1171 | 0.9530 | 0.9007 | 0.9690 |
| Sep08 | 0.0047 | 0.0005 | 0.0059 | -9.9999 | 0.7590 | 0.7140 | 0.1192 | 0.7543 | 0.7135 | ******** | 0.9273 | 0.8807 | 0.0112 |
| Sep08 | -0.0016 | -0.0013 | 0.0015 | 0.0021 | 0.7601 | 0.7149 | 0.1135 | 0.7617 | 0.7162 | 0.1118 | 0.9230 | 0.8722 | 1.0137 |
| Sep09 | -0.0016 | -0.0036 | 0.0009 | 0.0007 | 0.7626 | 0.7196 | 0.1194 | 0.7642 | 0.7202 | 0.1187 | 0.9180 | 0.8687 | 0.9541 |
| Sep09 | -0.0027 | -0.0014 | 0.0006 | 0.0010 | 0.7536 | 0.7092 | 0.1155 | 0.7563 | 0.7106 | 0.1145 | 0.9304 | 0.8778 | 0.9891 |
| Sep16 | -0.0033 | -0.0023 | 0.0011 | 0.0031 | 0.7500 | 0.7010 | 0.1270 | 0.7533 | 0.7033 | 0.1239 | 0.9354 | 0.8769 | 0.9138 |
| Sep16 | -0.0047 | -0.0029 | 0.0004 | 0.0013 | 0.7529 | 0.7025 | 0.1256 | 0.7576 | 0.7054 | 0.1245 | 0.9326 | 0.8719 | 0.9057 |
| Sep17 | -0.0038 | -0.0023 | 0.0000 | 0.0007 | 0.7501 | 0.7083 | 0.1278 | 0.7619 | 0.7106 | 0.1271 | 0.9252 | 0.8664 | 0.8866 |
| Sep17 | -0.0042 | -0.0030 | 0.0009 | 0.0011 | 0.7505 | 0.6995 | 0.1266 | 0.7547 | 0.7025 | 0.1255 | 0.9350 | 0.8747 | 0.8979 |
| Sep18 | -0.0037 | -0.0026 | 0.0005 | 0.0008 | 0.7541 | 0.7058 | 0.1275 | 0.7578 | 0.7076 | 0.1267 | 0.9284 | 0.8705 | 0.8858 |
| Sep18 | -0.0044 | -0.0032 | 0.0010 | 0.0008 | 0.7479 | 0.6970 | 0.1258 | 0.7523 | 0.7002 | 0.1250 | 0.9382 | 0.8760 | 0.9019 |
| Sep19 | -0.0040 | -0.0031 | 0.0005 | 0.0007 | 0.7552 | 0.7040 | 0.1269 | 0.7592 | 0.7071 | 0.1262 | 0.9204 | 0.8683 | 0.8913 |
| Sep19 | -0.0030 | -0.0031 | 0.0020 | 0.0014 | 0.7453 | 0.6930 | 0.1213 | 0.7433 | 0.6961 | 0.1199 | 0.9431 | 0.8809 | 0.9336 |
| Sep21 | -0.0052 | -0.0034 | 0.0006 | 0.0008 | 0.7315 | 0.6771 | 0.1107 | 0.7367 | 0.6805 | 0.1179 | 0.9633 | 0.8935 | 0.9533 |
| Sep21 | -0.0027 | -0.0025 | 0.0022 | 0.0019 | 0.7273 | 0.6706 | 0.1183 | 0.7300 | 0.6731 | 0.1164 | 0.9739 | 0.9017 | 0.9656 |
| Sep25 | -0.0052 | -0.0036 | 0.0002 | 0.0007 | 0.7271 | 0.6718 | 0.1165 | 0.7323 | 0.6754 | 0.1158 | 0.9670 | 0.8963 | 0.9661 |
| Sep25 | -0.0001 | -0.0038 | 0.0014 | 0.0009 | -9.9999 | 0.6691 | 0.1181 | -9.9598 | 0.6729 | 0.1172 | 0.9714 | -0.0656 | 0.9566 |
| Oct03 | -0.0028 | -0.0028 | 0.0020 | 0.0008 | -9.9999 | -9.9999 | -9.9999 | -9.9971 | -9.9971 | ******** | -0.0650 | -0.0653 | -0.0112 |
| Oct05 | -0.0037 | -0.0033 | 0.0020 | 0.0008 | 0.7290 | 0.6742 | 0.1122 | 0.7327 | 0.6775 | 0.1114 | 0.9579 | 0.8894 | 0.9999 |
| Oct05 | -0.0036 | -0.0041 | 0.0026 | 0.0007 | 0.7257 | 0.6723 | 0.1109 | 0.7293 | 0.6764 | 0.1102 | 0.9595 | 0.8936 | 1.0114 |
| Oct06 | -0.0050 | -0.0016 | 0.0019 | 0.0007 | 0.7300 | 0.6760 | 0.1113 | 0.7356 | 0.6806 | 0.1106 | 0.9529 | 0.8053 | 1.0065 |
| Oct06 | -9.9999 | -9.9999 | -9.9999 | -9.9999 | 0.7396 | 0.6072 | 0.1063 | ******** | ******** | ******** | 0.0607 | 0.0606 | 0.0110 |
| Oct07 | -0.0054 | -0.0045 | 0.0011 | 0.0007 | 0.7420 | 0.6904 | 0.1076 | 0.7474 | 0.6949 | 0.1069 | 0.9326 | 0.8707 | 1.0467 |
| Oct07 | -0.0054 | -0.0065 | 0.0019 | 0.0009 | 0.7414 | 0.6801 | 0.1073 | 0.7460 | 0.6946 | 0.1064 | 0.9330 | 0.8714 | 1.0456 |
| Oct09 | -0.0040 | -0.0043 | 0.0018 | 0.0007 | 0.7440 | 0.6910 | 0.1074 | 0.7496 | 0.6953 | 0.1067 | 0.9307 | 0.8669 | 1.0413 |
| Oct10 | -0.0045 | -0.0055 | 0.0025 | 0.0020 | 0.7400 | 0.6850 | 0.1075 | 0.7445 | 0.6905 | 0.1055 | 0.9365 | 0.8722 | 1.0524 |
| Oct11 | -0.0051 | -0.0018 | 0.0019 | 0.0007 | 0.7364 | 0.6034 | 0.1061 | 0.7415 | 0.6882 | 0.1054 | 0.9389 | 0.8751 | 1.05[illegible] |

Table 11, cont. NOX AND O3 CALIBRATIONS FOR 1984

16-May-1985

| DATE | NOX ZERO | NO ZERO | NO2 ZERO | O3 ZERO | NOX SPAN | NO SPAN | O3 SPAN | NOX RESP | NO RESP | O3 RESP | NO CAL | NOX CAL | O3 CAL |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oct11 | -0.0050 | -0.0044 | 0.0021 | 0.0022 | 0.7352 | 0.6833 | 0.1140 | 0.7402 | 0.6877 | 0.1118 | 0.9396 | 0.8766 | 0.9925 |
| Oct12 | -0.0060 | -0.0046 | 0.0010 | 0.0008 | 0.7372 | 0.6843 | 0.1134 | 0.7432 | 0.6889 | 0.1126 | 0.9373 | 0.8725 | 0.9848 |
| Oct12 | -0.0041 | -0.0048 | 0.0027 | 0.0008 | 0.7354 | 0.6813 | 0.1119 | 0.7395 | 0.6861 | 0.1111 | 0.9411 | 0.8768 | 0.9981 |
| Oct13 | -0.0035 | -0.0039 | 0.0024 | 0.0008 | 0.7413 | 0.6896 | 0.1137 | 0.7448 | 0.6935 | 0.1129 | 0.9304 | 0.8700 | 0.9815 |
| Oct13 | -0.0042 | -0.0046 | 0.0029 | 0.0008 | 0.7344 | 0.6807 | 0.1135 | 0.7386 | 0.6853 | 0.1127 | 0.9415 | 0.8773 | 0.9833 |
| Oct14 | -0.0029 | -0.0033 | 0.0029 | 0.0008 | 0.7409 | 0.6873 | 0.1130 | 0.7438 | 0.6906 | 0.1122 | 0.9336 | 0.8705 | 0.9870 |
| Oct14 | -0.0043 | -0.0046 | 0.0028 | 0.0007 | 0.7349 | 0.6806 | 0.1135 | 0.7392 | 0.6852 | 0.1128 | 0.9410 | 0.8759 | 0.9810 |
| Oct15 | -0.0031 | -0.0030 | 0.0027 | 0.0010 | 0.7560 | 0.7020 | 0.1155 | 0.7591 | 0.7050 | 0.1145 | 0.9139 | 0.8523 | 0.9666 |
| Oct23 | -0.0087 | -0.0074 | 0.0010 | 0.0007 | 0.6837 | 0.6344 | 0.1188 | 0.6924 | 0.6410 | 0.1181 | 0.9981 | 0.9290 | 0.9322 |
| Oct25 | -0.0091 | -0.0073 | 0.0000 | 0.0006 | -9.9999 | -9.9999 | 0.1147 | -9.9908 | -9.9926 | 0.1141 | -0.0640 | -0.0643 | 0.9637 |
| Oct25 | -0.0053 | -0.0055 | -0.0025 | 0.0010 | 0.6900 | 0.6455 | 0.1200 | 0.7033 | 0.6510 | 0.1190 | 0.9825 | 0.9133 | 0.9240 |

**Table 12.** NOx and O3 Auto-Calibrations for 1985

|  |  |  | DECAY= | 0 |  | DECAY= | 0 |
|---|---|---|---|---|---|---|---|
|  |  | INIT CAL | VAL NO= | 0.59568 | INIT CAL | VAL O3= | 0.12004 |
| 01-Jun-85 |  |  |  |  |  |  |  |
| DATE | DAYS | TIME | RESP IN | SPAN CAL | TIME | RESP IN | SPAN CAL |
| 21-Jun-85 | 20 | 300 | 6.0610 | 0.9828 | 300 | 1.0010 | 1.1992 |
| 21-Jun-85 | 20 | 1730 | 5.9788 | 0.9963 | 1730 | 0.9945 | 1.2070 |
| 25-Jun-85 | 24 | 300 | 5.9874 | 0.9949 | 300 | 1.0011 | 1.1991 |
| 26-Jun-85 | 25 | 300 | 5.9471 | 1.0016 | 300 | 1.0170 | 1.1803 |
| 26-Jun-85 | 25 | 1730 | 6.0261 | 0.9885 | 1730 | 1.0442 | 1.1496 |
| 28-Jun-85 | 27 | 300 | 6.0500 | 0.9846 | 300 | 1.0176 | 1.1797 |
| 08-Jul-85 | 37 | 300 | 1.1941 | 4.9885 | 300 | 1.0500 | 1.1432 |
| 08-Jul-85 | 37 | 1730 | 1.2643 | 4.7115 | 1730 | 0.9510 | 1.2622 |
| 09-Jul-85 | 38 | 300 | 5.9320 | 1.0042 | 300 | 0.9744 | 1.2320 |
| 10-Jul-85 | 39 | 300 | 5.8331 | 1.0212 | 300 | 1.0170 | 1.1803 |
| 10-Jul-85 | 39 | 1730 | 5.9195 | 1.0063 | 1730 | 0.9494 | 1.2643 |
| 05-Aug-85 | 65 | 300 | 6.0847 | 0.9790 | 300 | 1.0022 | 1.1977 |
| 12-Aug-85 | 72 | 400 | 6.0020 | 0.9925 | 400 | 0.9120 | 1.3162 |
| 15-Aug-85 | 75 | 300 | 5.8886 | 1.0116 | 300 | 0.9391 | 1.2782 |
| 16-Aug-85 | 76 | 300 | 5.8974 | 1.0101 | 300 | 0.9752 | 1.2309 |
| 16-Aug-85 | 76 | 1730 | 5.8836 | 1.0124 | 1730 | 1.0161 | 1.1813 |
| 20-Aug-85 | 80 | 300 | 5.9242 | 1.0055 | 300 | 1.0031 | 1.1967 |
| 20-Aug-85 | 80 | 1730 | 5.9472 | 1.0016 | 1730 | 1.0050 | 1.1944 |
| 23-Aug-85 | 83 | 300 | 6.0870 | 0.9786 | 300 | 0.9511 | 1.2621 |
| 23-Aug-85 | 83 | 1730 | 5.9740 | 0.9971 | 1730 | 0.9644 | 1.2447 |
| 28-Aug-85 | 88 | 300 | 5.9622 | 0.9991 | 300 | 1.0080 | 1.1908 |
| 29-Aug-85 | 89 | 300 | 5.9767 | 0.9967 | 300 | 1.0372 | 1.1574 |
| 29-Aug-85 | 89 | 1730 | 6.0259 | 0.9885 | 1730 | 1.0556 | 1.1372 |
| 04-Sep-85 | 95 | 1730 | 5.9463 | 1.0018 | 1730 | 1.1110 | 1.0804 |
| 06-Sep-85 | 97 | 1730 | 5.9095 | 1.0080 | 1730 | 1.0971 | 1.0942 |
| 11-Sep-85 | 102 | 1730 | 5.8820 | 1.0127 | 1730 | 1.0220 | 1.1745 |
| 01-Oct-85 | 122 | 300 | 6.0835 | 0.9792 | 300 | 1.0550 | 1.1378 |
| 01-Oct-85 | 122 | 1730 | 5.9669 | 0.9983 | 1730 | 1.0200 | 1.1768 |
| 17-Oct-85 | 138 | 300 | 6.2986 | 0.9457 | 300 | 1.0700 | 1.1219 |
| 17-Oct-85 | 138 | 1730 | 6.0657 | 0.9820 | 1730 | 1.0200 | 1.1768 |
|  |  | AVE RESPONSE= |  | 5.983607 0.995737 |  | 1.009376 | 1.191563 |
|  |  | AVE MAN CAL= |  | 0.995512 |  | 1.18923 |  |
|  |  | AVE CAL VAL= |  | 0.595675 |  | 0.120038 |  |

factor. The different types of calibration sources and the documentation, forms, and data bases associated with this processing were described above. This section discusses in more detail the procedures of processing the calibration data.

Figure 11 shows the flowchart for HC calibration data processing with CALENTRY events indicated. Table 13 shows the RUNENTRY events flowchart.

### *Identification of Calibration Chromatogram and Calibration Source*

If one or more forms of documentation indicate that a calibration(s) was performed, then the first step is to identify the data and calibration source(s). If the calibration was performed during an experiment, it was logged in CALENTRY when the experiment was logged in RUNENTRY. Otherwise, the run calendars indicate a calibration event and the presence of a new calibration folder. If the calibration occured during an experiment, the run folder INSTRUMENT INVENTORY CHECKLIST indicates the instruments calibrated, otherwise, the stripcharts present in the calibration folder indicate which instruments were calibrated. Calibration sources are identified on the stripcharts.

### *Issue Calibration Pick Instructions*

Calibration processing (pick) instructions are given by the PC via the CAL PICK INSTRUCTION form. The form is stored in the CAL PICK INSTRUCTION NOTEBOOK by date. The fact that pick instructions are given is entered into CALENTRY. Several QA steps occur at this point. Documentation is checked for reasonableness and completeness (sources, chart settings, instrument settings). The chromatograms are inspected for reasonableness (match standard example chromatograms with source for conditions specified).

### *Official Calibration Sources/ OCS Report*

The raw data can be processed (picked), but before final processing can occur, the calibration source data must be validated and entered into the OFFICIAL CALIBRATION SOURCE (OCS) DATATRIEVE database and the OCSFIL.DAT updated. The forms used for recording the OCS data were discussed above.

Several sources are used throughout the season. These were listed above. The validation procedure was also reported. The first step is to check the report from the OCS database to see if the source has been entered. If the OCS does not exist then it must be created or at least validated. The details of processing single (used once) OCS are discussed next. The OCS report is listed in Appendix C.

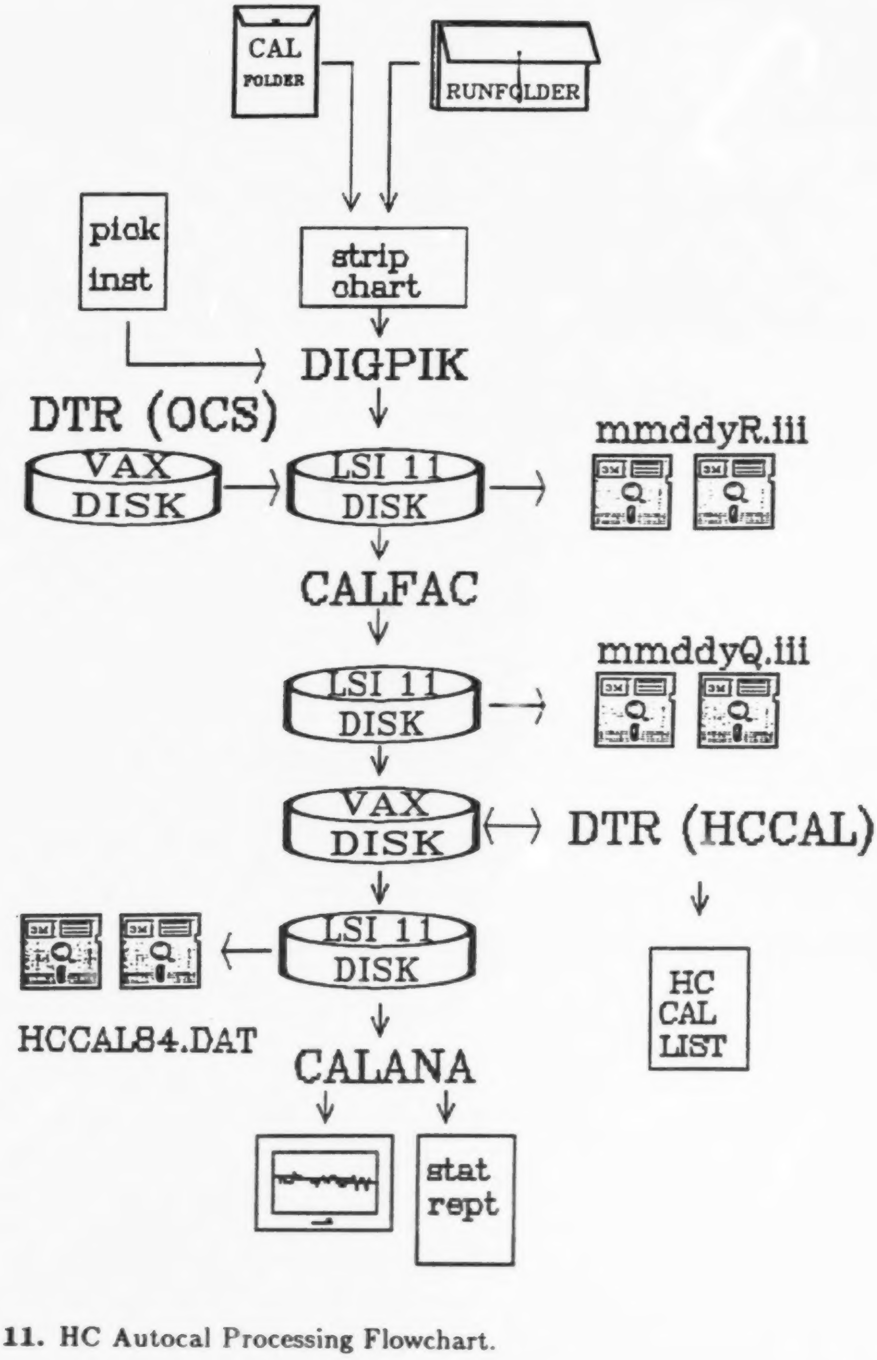

CAL
FOLDER
RUNFOLDER
pick
inst
strip
chart
DIGPIK
DTR (OCS)
VAX
DISK
LSI 11
DISK
mmddyR.iii
CALFAC
LSI 11
DISK
mmddyQ.iii
VAX
DISK
DTR (HCCAL)
LSI 11
DISK
HCCAL84.DAT
HC
CAL
LIST
CALANA
stat
rept

**Figure 11.** HC Autocal Processing Flowchart.

## Table 13.
## Processing System for Instrument Auto-Calibration Data

```
tot inst    cal analysis
      \    /            \
       !CPI!            !OCS!
           \                \
            \                \
             <DPR>----------<CFR>--(Q2V)--(DTR)--(C2L)--<CLR>--!CQA!
```

!sss! == stages determined by Project coordinator (PC)
<sss> == stages determined by Peak Pickers (PP)
(sss) == stages determined by Computer Techs (CT)

| Step | CALENTRY stages | Meaning |
|---|---|---|
| PC | CPI : CAL pick Inst | Charts marked, cal status sheet in |
| PP | DPR : Digpik run | Cal data digitized and R-file exists |
| PC | OCS : OCS ok | Official Cal Source exists in DTR |
| PP | CFR : CALFAC run | Cal Factor computed, Q-file created |
| CT | Q2V : Qfile to vax | Q-file moved to VAX |
| CT | DTR : DTR file updated | Cal Data added to DTR data base |
| CT | C2L : Cals to LSI | DTR CAL file loaded on LSI-11 |
| PP | CLR : CALANA run | Cal Factors analyzed |
| PC | CQA : Cal QA | Cal Factor Quality Assurance |
| PC | NTB : Not to be proc | Not to be processed |
| PC | BAD : Stop processing | Something is wrong with this run |

### *Create OCS for Single Injection*

These OCS are created in the smog chamber. The amounts of HC that are injected are documented along with the chamber temperature in the calibration folders or on the RUN SHEET. A LOTUS 123 database/spreadsheet OCSIC (described above) is used to process this information. The species id number is used to look up all the necessary species specific information (density, molecular weight, carbon number, *etc.*) and the program calculates and records the ideal concentration. Table 4 lists the OCSIC report. All OCS information is recorded on OCS forms and recorded in the OCS notebook as described above. The validated OCS concentrations are entered into the DATATRIEVE database CAL_SOURCES_FMS. A database report procedure is used to update the `OCSFIL.DAT` which is transfered to the LSI to await final processing. The fact that the OCS exists is entered into the DATATRIEVE CALENTRY database.

### *Run DIGPIK on calibration Data to Make R-files*

Once calibration processing instructions have been given, raw data are picked using a program on the LSI (DIGPIK) where the data are digitized and a response file (`R-file`, `MMDDYR.iit`) is produced. The files are backed-up (copied) onto floppies.

### *Run CALFAC to Calculate Calibration Factors*

Once the response data has been picked and the OCS data has been updated to `OCSFIL.DAT`, the calibration factor can be calculated. A program on the LSI CALFAC is run which reads the internal documentation in the response file `R-file` and compares the data with the appropriate OCS to generate the concentration per response unit calibration factor. A QA step is performed here. The calibration factors are inspected and reviewed in context with the existing database with the program CALLOK which plots or lists the data vs. julian date with a linear least-squares fit. The program identifies calibration data which varies by more than a specified percentage. The generated calibration data is output in files ("Q"-files) specific for the instrument and the day calibrated. These files are backed-up on floppy.

The Q-files are transferred and updated to the DATATRIEVE HC_CAL database if the calibration data seems reasonable. A DATATRIEVE report procedure PRINT_HC_CAL_FACTORS, is run to generate an updated calibration list sorted by instrument, species, and date. All data are converted to a single specified attenuation for easy inspection. Another DATATRIEVE procedure, PRINT_FILE_CALANA, is used to generate another file which is then transfered to the LSI-11/23 computer to be used by a program called CALANA which performs a statistical and graphical analysis of the calibration database.

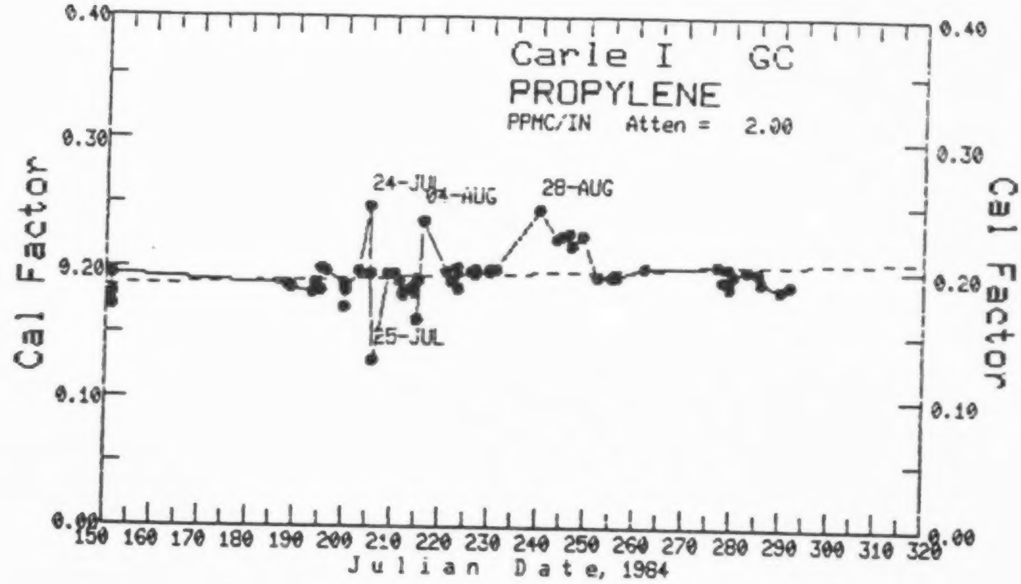
We expect a certain amount of noise or variation based on experience. Usually the calibration factors are very stable with little or no trend demonstrated. Variations are found, however, and some are real indications of instrument change. Discrepancies that are more than a few percent are investigated. Figure 12 shows example CALANA plots and statistical reports. Appendix D contains a larger collection of these plots and statistics.

The statistical report first lists the data range searched in the database. The number of data points found and included for the analysis are listed. The slope and intercept of the straight line fit through the data are listed with the standard deviation and relative standard deviation for each. The correlation coefficient is also listed. The minimum, maximum and mean of the data are shown with the standard deviation and relative standard deviation. Lastly the equation of the straight line fit is shown. Table 14 and Table 15 show a compilation of the statistics from this set.

This analyses from all of the CALANA plots and reports show that little or no trend was observed in the data. If the line was perfectly horizontal, the correlation factor would be 0.0. Table 14 shows the means, standard deviations, and relative standard deviations for the more complete data set shown in Appendix D. For the 1984 season the average relative standard deviation is just under 10 percent with a standard deviation of 2.2 percent. For the 1985 season the average relative standard deviation is 6.6 percent percent with a standard deviation of 3.5 percent. This suggests the uncertainty in the data would be about 10% *if the calibration factors were used straight from the initial processing and no additional information and QA techniques were used to check and tune the calibration data.* Because specific calibration factors are used and because the data are subjected to further examination and adjustment, the uncertainty in the final data is less than 10%.

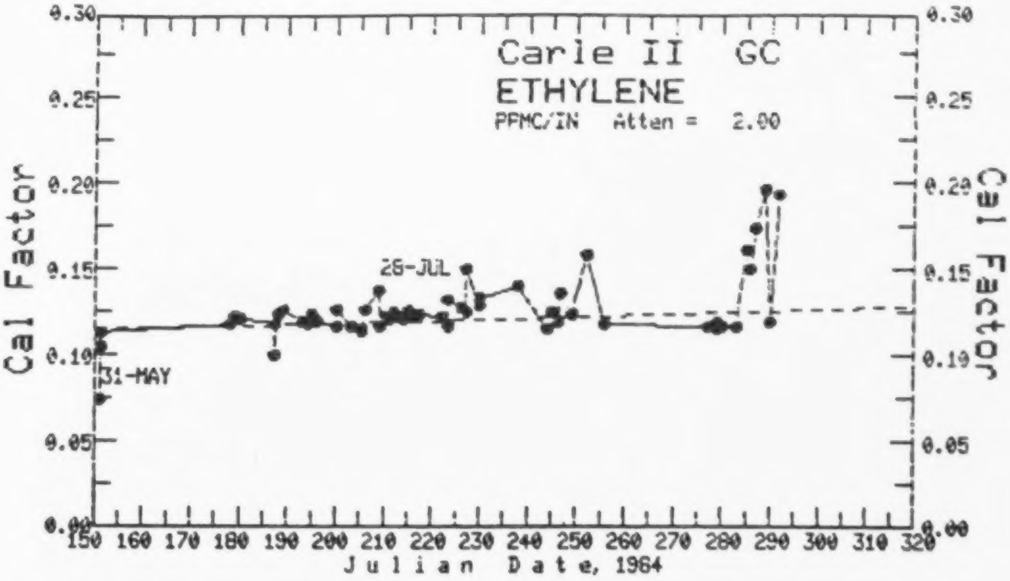
Valid deviations can be caused by many factors, including variation in the instrument operating characteristics. Calibration factors specific to the current instrument status should be used rather than some average value. Non-valid sources f calibration data deviation include improper processing. Many QA measures are ken to prevent these errors. These measures will be discussed further.

There are several explanations for variation in calibration data. Insufficient sample flow of calibration gases, will result in very low responses and consequently very large (incorrect) calibration factors. Sometimes the instrument operating conditions change (*e.g.* carrier flow) which changes the peak width and consequently the calibration factor. For example, this happened in late August 1985 to the Carle II



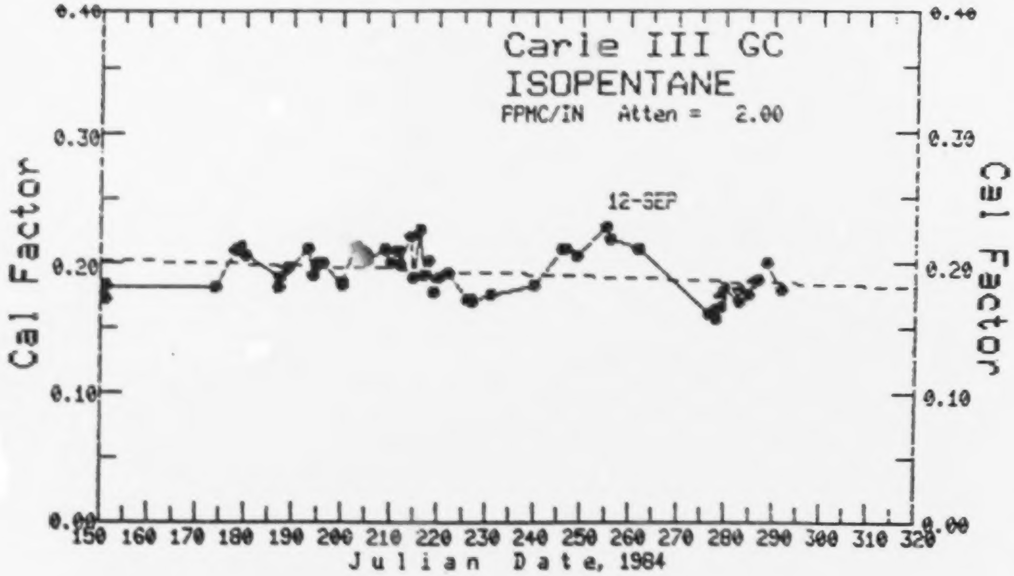
```
For the species PROPYLENE and the instrument Carle I   GC:

Beginning Caldate:               30-MAY-84
                          Day:   150
Ending     Caldate:              16-NOV-84
                          Day:   320
Upper CalFactor Limit                0.40000
Lower CalFactor Limit                0.00000

The number of data points           62
The number included   was           62
The slope of this fit  is 1.3522654E-004
         with a std dev of 6.6911662E-005   rel. dev = 49.5 %
The intercept is          1.6694184E-001
         with a std dev of 1.5341250E-002   rel. dev = 9.2 %
The std dev of the fit is 1.8079919E-002   PE =  0.01205
The correlation coeff is   0.25246

The min, mean, max are        0.13040,     0.19760,     0.25009
The standard deviation is  0.01853   rel. dev = 9.4 %

Cal =  0.00014 X (Julian Date - 150) +  0.18723
```

**Figure 12.** CALANA Example Figures.



```
For the species ETHYLENE and the instrument Carle II  GC:

Beginning Caldate:          30-MAY-84
                      Day:  150
Ending     Caldate:         16-NOV-84
                      Day:  320
Upper CalFactor Limit          0.14000
Lower CalFactor Limit          0.00000

The number of data points      61
The number included  was       53
The slope of this fit  is 7.7424523E-005
      with a std dev of 3.6302085E-005   rel. dev = 46.9 %
The intercept is          1.0432247E-001
      with a std dev of 7.9898236E-003   rel. dev = 7.7 %
The std dev of the fit is 8.8857276E-003  PE =  0.00592
The correlation coeff is   0.28616

The min, mean, max are        0.07444,     0.12116,     0.19795
The standard deviation is  0.00918   rel. dev = 7.6 %

Cal =  0.00008 X (Julian Date - 150) +  0.11594
```

**Figure 12, cont.** CALANA Example Figures.



```
For the species ISOPENTANE and the instrument Carle III GC:

Beginning Caldate:            30-MAY-84
                      Day:   150
Ending    Caldate:            16-NOV-84
                      Day:   320
Upper CalFactor Limit           0.40000
Lower CalFactor Limit           0.00000

The number of data points       60
The number included   was       60
The slope of this fit  is -1.222656E-004
      with a std dev of 5.6003271E-005   rel. dev = -45.8 %
The intercept is          2.2209272E-001
      with a std dev of 1.2738738E-002   rel. dev = 5.7 %
The std dev of the fit is 1.6698649E-002   PE =  0.01113
The correlation coeff is  -0.27557

The min, mean, max are       0.15986,    0.19468,    0.23074
The standard deviation is  0.01722   rel. dev = 8.8 %

Cal = -0.00012 X (Julian Date - 150) +  0.20375
```

**Figure 12, cont.** CALANA Example Figures.

## Table 14

## Summary of CALANA Statistics for 1984

| Carle I | MIN | MAX | MEAN | STD DEV | REL STD D |
|---|---|---|---|---|---|
| propylene | 0.130 | 0.250 | 0.198 | 0.019 | 9.4% |
| isopentane | 0.140 | 0.196 | 0.158 | 0.010 | 6.3% |
| Carle II | | | | | |
| ethylene | 0.074 | 0.198 | 0.121 | 0.009 | 7.6% |
| ethane | 0.013 | 0.231 | 0.147 | 0.007 | 5.0% |
| propylene | 0.369 | 0.976 | 0.553 | 0.054 | 9.8% |
| propane | 0.428 | 1.059 | 0.607 | 0.060 | 9.9% |
| Carle III | | | | | |
| 1-butene | 0.074 | 0.130 | 0.100 | 0.011 | 11.5% |
| n-butane | 0.053 | 0.131 | 0.102 | 0.016 | 11.7% |
| cis-2-butene | 0.070 | 0.127 | 0.105 | 0.015 | 14.0% |
| trans-2-butene | 0.091 | 0.132 | 0.115 | 0.011 | 9.2% |
| 1,3-butadiene | 0.090 | 0.137 | 0.116 | 0.012 | 9.9% |
| isopentane | 0.160 | 0.231 | 0.195 | 0.017 | 8.8% |
| n-pentane | 0.228 | 0.347 | 0.289 | 0.028 | 9.8% |
| benzene | 0.080 | 0.106 | 0.090 | 0.009 | 10.3% |
| toluene | 0.114 | 0.167 | 0.137 | 0.014 | 10.0% |
| m-xylene | 0.187 | 0.269 | 0.225 | 0.027 | 12.0% |
| o-xylene | 0.256 | 0.318 | 0.281 | 0.024 | 8.7% |
| methanol | 0.835 | 1.206 | 1.050 | 0.143 | 13.7% |
| ave | | | | | 9.9% |
| std dev | | | | | 2.2% |

# Table 15

## Summary of CALANA Statistics for 1985

| Carle I | MIN | MAX | MEAN | STD DEV | REL STD D |
|---|---|---|---|---|---|
| propylene | 0.201 | 0.323 | 0.220 | 0.007 | 3.3% |
| isopentane | 0.169 | 0.267 | 0.187 | 0.018 | 9.5% |
| Carle II | | | | | |
| ethylene | 0.111 | 0.140 | 0.122 | 0.006 | 4.9% |
| ethane | 0.134 | 0.215 | 0.157 | 0.021 | 13.2% |
| propylene | 0.461 | 0.734 | 0.533 | 0.066 | 12.4% |
| propane | 0.532 | 0.829 | 0.614 | 0.082 | 13.3% |
| Carle III | | | | | |
| 1-butene | 0.069 | 0.081 | 0.078 | 0.003 | 3.7% |
| n-butane | 0.079 | 0.094 | 0.085 | 0.004 | 5.0% |
| cis-2-butene | 0.081 | 0.091 | 0.086 | 0.003 | 3.1% |
| trans-2-butene | 0.085 | 0.105 | 0.094 | 0.004 | 3.8% |
| 1,3-butadiene | 0.083 | 0.099 | 0.092 | 0.003 | 3.3% |
| isopentane | 0.153 | 0.187 | 0.166 | 0 006 | 3.6% |
| n-pentane | 0.229 | 0.267 | 0.245 | 0.010 | 3.9% |
| benzene | 0.071 | 0.091 | 0.081 | 0.006 | 7.1% |
| toluene | 0.088 | 0.133 | 0.122 | 0.010 | 8.3% |
| m-xylene | 0.180 | 0.226 | 0.197 | 0.016 | 7.9% |
| o-xylene | 0.249 | 0.292 | 0.265 | 0.016 | 6.0% |
| ave | | | | | 6.6% |
| std dev | | | | | 3.5% |

gas-chromatograph. The effect is larger for compounds with longer retention times (compare propylene with ethylene, which elutes almost immediately after injection). The formaldehyde instrument (CEA 555) is dependent on the air-sample flowrate. Low flowrates resulted in loss of sensitivity (low response) and consequently high calibration factors for June 21 and August 20, 1985 for example. Although these calibration factors are far from the mean, they are correct and must be used in data processing. Incorrectly recorded attenuation will, of course, cause generated calibration data to be off by a factor of multiples of 2 or 10. The Perkin Elmer Sigma 10 integrator which yields areas not affected by the GC attenuation settings, can be compared with areas of calibrations performed on other days to determine if this type of problem has occurred; the attenuation can be corrected in the "R" file and reprocessed.

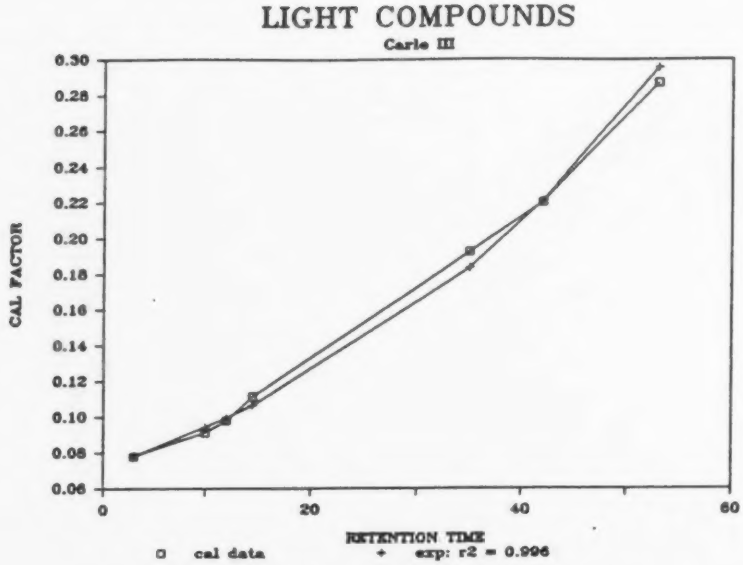
### *Estimation of Calibration Factors for Infrequently Calibrated* HC

The technique discussed above requires an explicit calibration source for the compound being monitored to generate a calibration factor. Sometimes calibration data is sparse or the species to be processed has no explicit calibration source. There are several techniques for establishing appropriate calibration factors. These are often used together.

When sufficient supporting calibration data exists, a plot of the calibration factors of well calibrated compounds measured on the same column, as a function of retention time, can be least-squares fit to an exponential function. A LOTUS 123 spreadsheet called CALEXTR is used for this. Figure 13 shows plots for the two columns in the Carle III GC. Our experience has been that good fits are obtained. The calibration factor for the uncalibrated compound can be estimated by locating its retention time on the curve. The ratios of the frequently calibrated compounds to the less frequently calibrated compounds can be determined for future needs. If integrator data is available, a check is done using integrator areas ratioed to the estimated concentrations of all the compounds.

If the compound requiring a calibration factor is part of a well characterized mixture (the source), the concentrations of the other compounds can be used to determine the concentration of the compound in question by ratios. The calibration factor can then be calculated.

If reliable integrator data is available, the area count can be calibrated with any known calibration sources, and the corrected area used to determine the concentration of the uncalibrated compound. The concentration can then be used to calculate the calibration factor for the picked data.



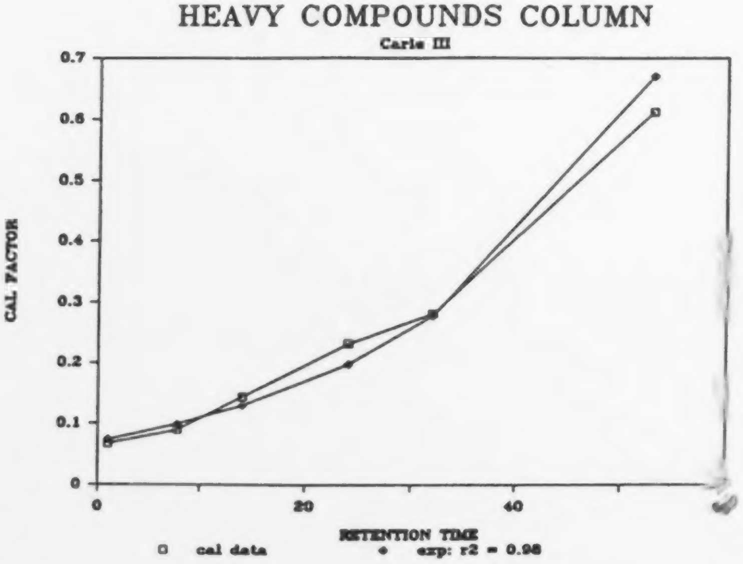


**Figure 13.** Calextr Examples.

If good calibration data exists for all species at some time, ratios of less frequently calibrated species to frequently calibrated species can be determined. These ratios can be used to calculate calibration factors for times when the calibration data are less complete.

### *Final Calibration Factor Calculations*

To process data, calibration factors can be taken from the **HCCAL DATATRIEVE** report for explicit calibrations or extrapolated from calibration data for other species. Calibrations may not have been performed the day of an experiment for all species. Interpolation may be needed between the calibrations for a species done right before and after the day in question.

The discussion to this point has been concerned with the processing of calibration data and using calibration data to estimate calibration factors for compounds not explicitly calibrated. Calibration factors need additional checking and perhaps adjustment sometimes before they are applied to process data. These checking procedures are actually QA steps performed in experimental data processing but are definitely part of calibration data processing.

Once calibration factors are calculated, they are applied to the raw experimental data. The resulting concentration data should fit with the known target conditions, the amounts injected, and the known resulting conditions of other similar experiments. The data should also yield the same composition as determined by analytical data for other similar experiments. This should occur with calibration factors used which are at least similar to those used to process experiments conducted before and after the experiment in question (see discussion of **RUN_CAL_USED**). Ratios of initial conditions should be somewhat consistent with integrator areas when peaks are reasonably well defined and integrateable. The calibrated integrator area should be consistent with peak height derived concentration data for large peaks with good resolution and clean base lines.

# 4

# Experimental Data

This chapter presents the procedures, tools, and techniques for processing the experimental data. Sections will discuss documentation, data processing tracking systems, and how data are actually processed.

## Experimental Results Documentation

Documentation of experimental conditions and results is performed at every level of processing to assure that no data or other useful information is lost and that all data can be processed. Methods have been developed to allow for redundant documentation and to provide the smog chamber operators several different opportunities to document the experiment.

### Data

Data are documented several ways reflecting the different types of data acquisition techniques. Data is acquired and recorded by both computer and stripchart. Printouts are also produced by the computer during and after an experiment and provide additional documentation.

#### *Stripcharts*

Almost every source of data is recorded on stripchart, providing a backup for the computer DA system in case of failure. For instruments that produce data not suitable for the computer DA system, stripchart recorders are the main data acquisition device. All stripcharts are documented with rundate, instrument, time, side, attenuation, chart speed, full scale deflection, and calibration information. Documentation of stripcharts is requested by the setup checklist and performed by the setup operator. Changes of instrument settings or conditions are noted directly on the stripchart during the experiment. Time and side is recorded several times throughout the experiment, as requested by all of the checklists discussed above. A pack-up inventory checklist assures that all stripcharts are collected and stored in the runfolder. Stripchart data is obtained for the following instruments:

- $O_3$ monitor
- $NO_x$ monitor
- Carle 1 GC-FID for HC
- Carle 2 GC-FID for HC
- Carle 3 GC-FID for HC
- Formaldehyde monitor
- Dewpoint monitor
- Varian GC (PAN, tracers, nitrates, biacetyl)
- PE900 GC
- TSR (total solar radiation)/UV sensors

### *Printouts*

Printouts produced during and after an experiment also document the experimental data. These are retained in each runfolder:

- `PRINT PROFILE`—computer data dump during run
- Experiment `COMMAND FILE` listing—list of scheduled injections and chamber control commands
- Experiment `BAKTRN FILE` listing—list of actual injections and chamber control commands (both scheduled and manually activated)
- Operator's `REMARKS FILE`- comment file

### *Computer Data*

There are two types of computer data generated by this data processing system: computer data acquired during the experiment and files produced from stripchart recorded data after the experiment. Documentation for computer data exists within the data files produced themselves. Time, instrument, side, and any intermediate conversion factors used to store the data is recorded automatically. The remarks file contains comments entered by the site operators before, during, and after the experiment directly into the computer, which are automatically documented with time entered. The data files produced from stripchart data after the experiment contain all of the documentation recorded on the stripcharts and the name of the people involved in processing the data.

## Forms

Several paper forms are used to help document the experimental conditions and resulting data. Several of these are filled out at the smog chamber site as the experiment is set up and executed.

### *Run Form*

The run form is a major documenting tool. It is used to record all the information needed to determine what experiment was attempted, what the chamber conditions were, time the experiment starts and ends, and important notes about the experiment actually conducted. The form is partially filled out before the experiment to officially record the desired target conditions including sources and amounts of chemical species. The morning operator takes instructions from this form to initiate the experiment, and records important comments about chamber conditions, deviations from target conditions, and any problems. This form is shown in Figure 14.

### *Instrument Checklist Form*

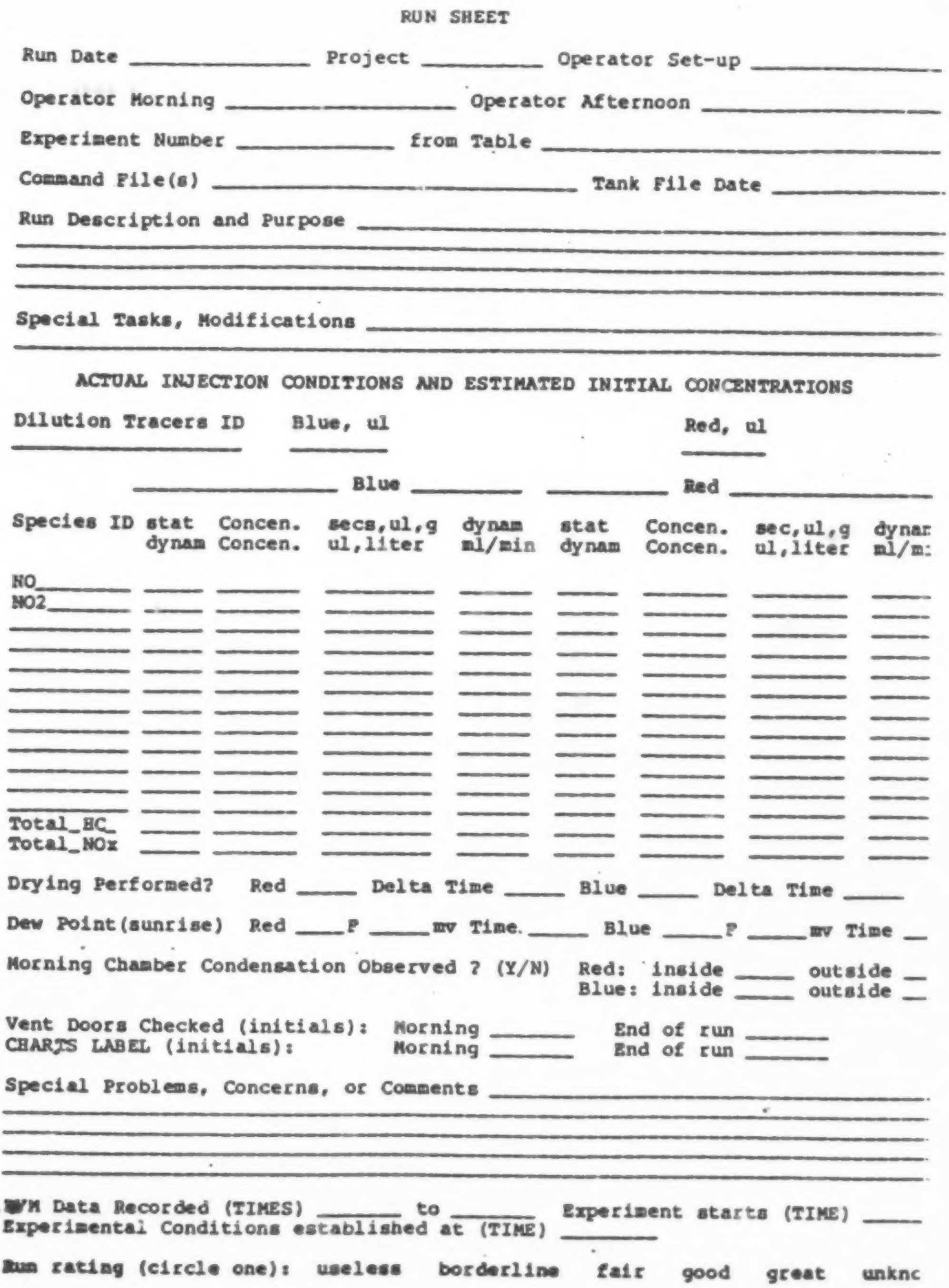
The instrument checklist is filled out the morning of the experiment and is attached to the run form. It is used to indicate which instruments are operational and were used, any calibrations performed, and any problems with the instruments themselves. This form is shown in Figure 15.

### *Run Folder Inventory Checksheet Form*

This form is used to inventory the run folders contents when the runfolder is first logged into the data processing system. It is a primary QA step used in conjunction with the instrument checklist form to determine what data exists, including documentation. Login and filling out of this form occurs before anyone is allowed to work with the contents. This form is shown in Figure 16.

### *Data Processing Instruction Form*

The data processing instruction form is used to collect and convey important information about the data collected on stripcharts during an experiment. It is an intermidiate documenting tool used to indicate start and stop times of valid data, calibration data (not to be confused and picked as run data), species to pick and problems in general with the data. Calibration factors and any calculations or notes are indicated on this form. The information on this form eventually ends up in the final segmented file used for distribution. This form is shown in Figure 17.



RUN SHEET

Run Date ____ Project ____ Operator Set-up ____

Operator Morning ____ Operator Afternoon ____

Experiment Number ____ from Table ____

Command File(s) ____ Tank File Date ____

Run Description and Purpose ____

Special Tasks, Modifications ____

ACTUAL INJECTION CONDITIONS AND ESTIMATED INITIAL CONCENTRATIONS

Dilution Tracers ID ____ Blue, ul ____ Red, ul ____

____ Blue ____ ____ Red ____

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Species ID | stat dynam | Concen. Concen. | secs,ul,g ul,liter | dynam ml/min | stat dynam | Concen. Concen. | sec,ul,g ul,liter | dynar ml/m: |
| NO | | | | | | | | |
| NO2 | | | | | | | | |
| | | | | | | | | |
| | | | | | | | | |
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| | | | | | | | | |
| | | | | | | | | |
| Total_HC_ | | | | | | | | |
| Total_NOx | | | | | | | | |

Drying Performed? Red ____ Delta Time ____ Blue ____ Delta Time ____

Dew Point(sunrise) Red ____F ____mv Time ____ Blue ____F ____mv Time ____

Morning Chamber Condensation Observed ? (Y/N) Red: inside ____ outside ____
Blue: inside ____ outside ____

Vent Doors Checked (initials): Morning ____ End of run ____
CHARTS LABEL (initials): Morning ____ End of run ____

Special Problems, Concerns, or Comments ____

WM Data Recorded (TIMES) ____ to ____ Experiment starts (TIME) ____
Experimental Conditions established at (TIME) ____

Run rating (circle one): useless borderline fair good great unknc

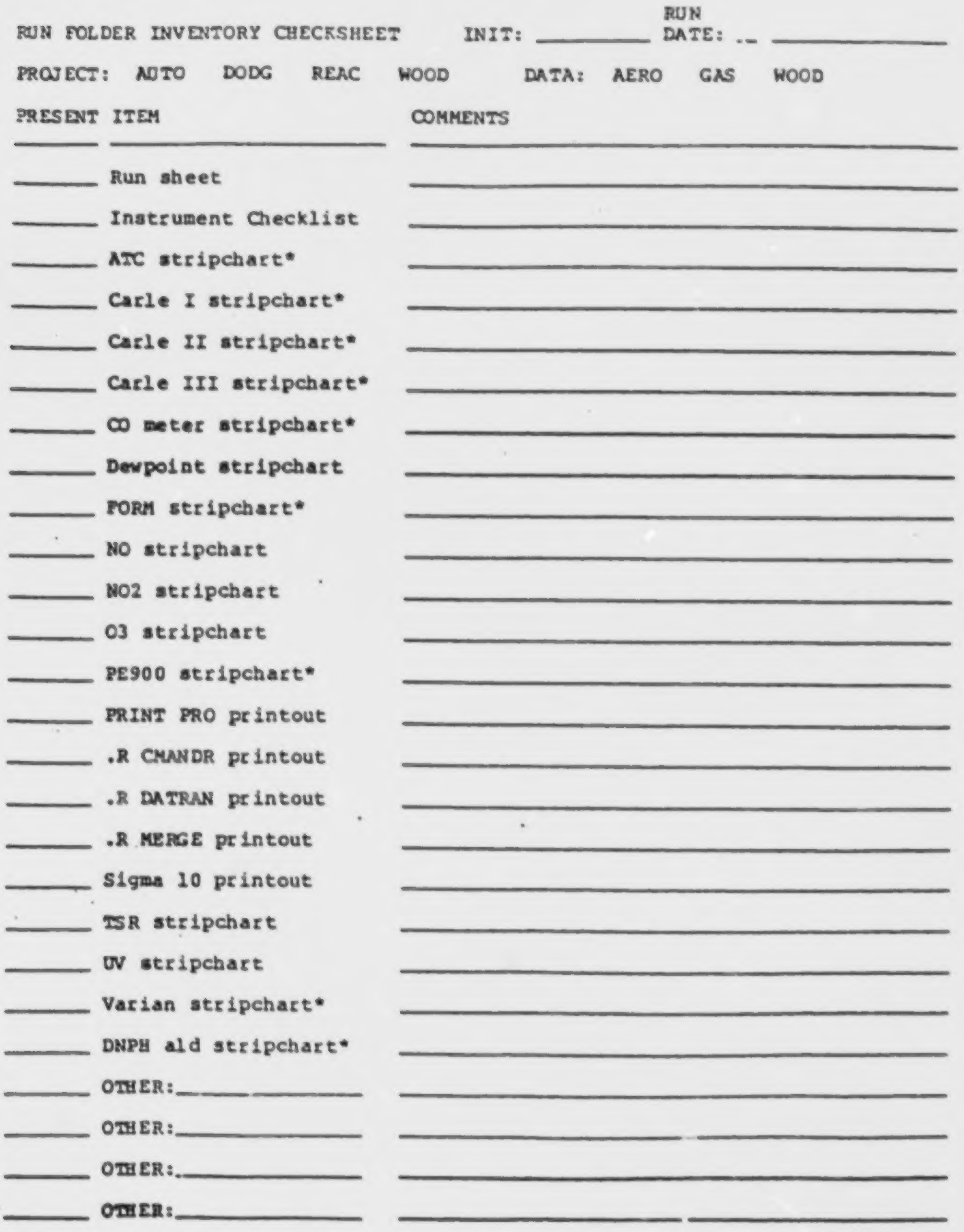
Figure 14. Runsheet

Instrument Checklist Run Date ____________

| Instrument | Cal Today (y/n) (type) | Cal TIME(S) | Operational (check) | Not Operational (check) | Not Used (check) | Data Acquisition QA (init.) | Note (num) |
|---|---|---|---|---|---|---|---|
| ATC | | | | | | | |
| Carle I | | | | | | | |
| Carle II | | | | | | | |
| Carle III | | | | | | | |
| CEA Formaldehyde | | | | | | | |
| CO meter | | | | | | | |
| Dew Point | | | | | | | |
| DNPH Aldehydes | | | | | | | |
| Nitric Acid | | | | | | | |
| NOx Bendix | | | | | | | |
| Ozone Bendix | | | | | | | |
| PE 900 (chamber) | | | | | | | |
| Saltzman | | | | | | | |
| Temp | | | | | | | |
| TSR | | | | | | | |
| UV | | | | | | | |
| Varian aerosol | | | | | | | |
| Varian gas | | | | | | | |
| PAN | | | | | | | |
| Nitrates | | | | | | | |
| Tracer | | | | | | | |
| Other | | | | | | | |
| Other | | | | | | | |
| Other | | | | | | | |
| Other | | | | | | | |

# Notes

Figure 15. Instrument Checklist Form



RUN FOLDER INVENTORY CHECKSHEET INIT: ________ RUN DATE: ____________

PROJECT: AUTO DODG REAC WOOD DATA: AERO GAS WOOD

PRESENT ITEM COMMENTS

_______ Run sheet ____________________

_______ Instrument Checklist ____________________

_______ ATC stripchart* ____________________

_______ Carle I stripchart* ____________________

_______ Carle II stripchart* ____________________

_______ Carle III stripchart* ____________________

_______ CO meter stripchart* ____________________

_______ Dewpoint stripchart ____________________

_______ FORM stripchart* ____________________

_______ NO stripchart ____________________

_______ NO2 stripchart ____________________

_______ O3 stripchart ____________________

_______ PE900 stripchart* ____________________

_______ PRINT PRO printout ____________________

_______ .R CMANDR printout ____________________

_______ .R DATRAN printout ____________________

_______ .R MERGE printout ____________________

_______ Sigma 10 printout ____________________

_______ TSR stripchart ____________________

_______ UV stripchart ____________________

_______ Varian stripchart* ____________________

_______ DNPH ald stripchart* ____________________

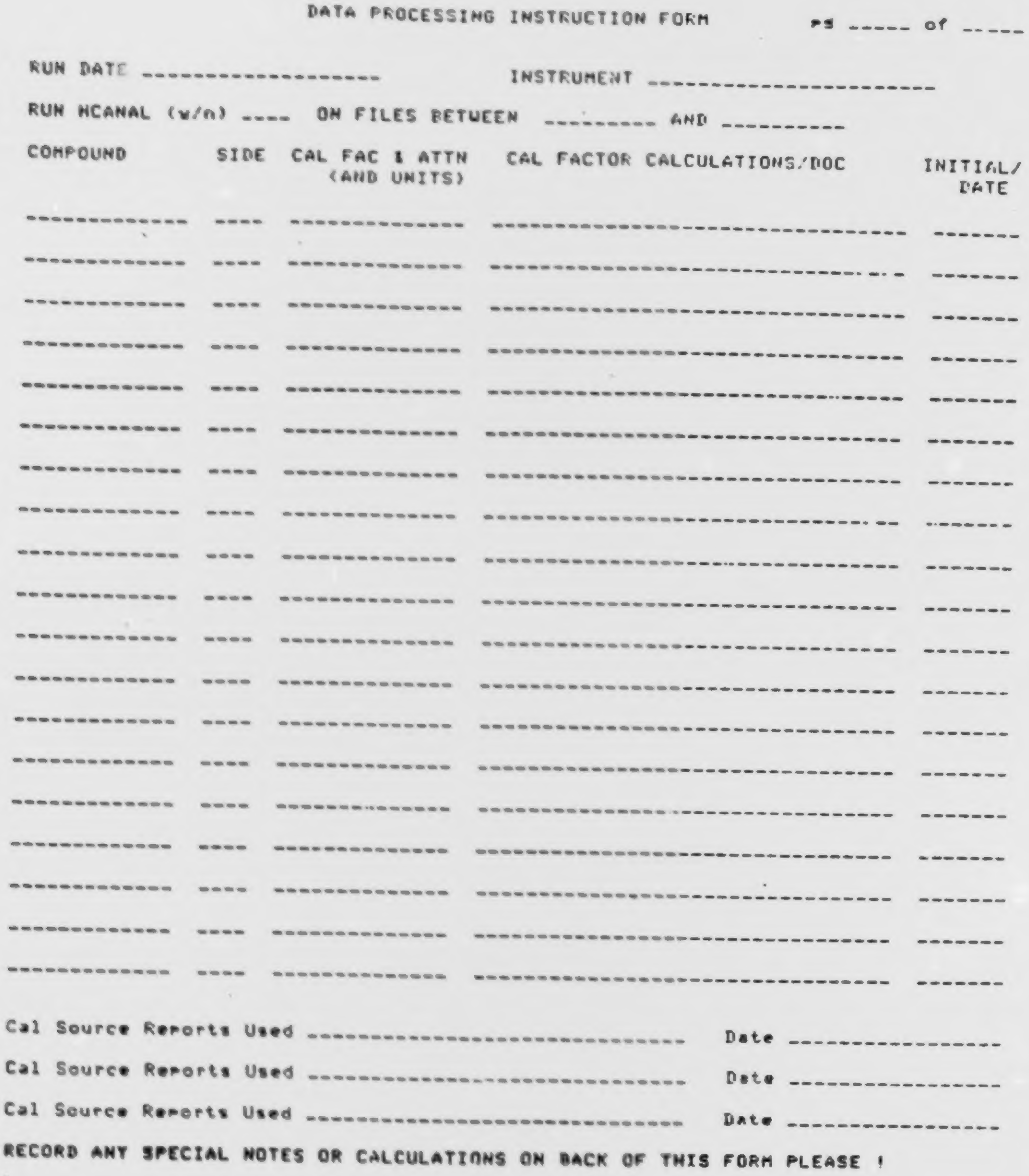
_______ OTHER:__________ ____________________

_______ OTHER:__________ ____________________

_______ OTHER:__________ ____________________

_______ OTHER:__________ ____________________

Figure 16. Run Folder Inventory Checksheet Form



DATA PROCESSING INSTRUCTION FORM pg ----- of -----

RUN DATE ------------------ INSTRUMENT ----------------------

RUN NCANAL (y/n) ---- ON FILES BETWEEN --------- AND ----------

| COMPOUND | SIDE | CAL FAC & ATTN (AND UNITS) | CAL FACTOR CALCULATIONS/DOC | INITIAL/ DATE |
|---|---|---|---|---|
| ------------ | ---- | ------------- | -------------------------------- | ------- |
| ------------ | ---- | ------------- | -------------------------------- | ------- |
| ------------ | ---- | ------------- | -------------------------------- | ------- |
| ------------ | ---- | ------------- | -------------------------------- | ------- |
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| ------------ | ---- | ------------- | -------------------------------- | ------- |
| ------------ | ---- | ------------- | -------------------------------- | ------- |
| ------------ | ---- | ------------- | -------------------------------- | ------- |

Cal Source Reports Used ----------------------------- Date ----------------

Cal Source Reports Used ----------------------------- Date ----------------

Cal Source Reports Used ----------------------------- Date ----------------

RECORD ANY SPECIAL NOTES OR CALCULATIONS ON BACK OF THIS FORM PLEASE !

**Figure 17.** Data Processing Instruction Form

### *DVMFIX Data Sheet Form*

This form is similar to the Data Processing Instruction Form used with stripchart data. It is used to record and convey important information required to properly process the data recorded with the DVM computer acquisition system. Calibration factors, periods of valid data, and general documentation are indicated here. The information on this form eventually ends up in the final segmented file used for distribution. This form is shown in Appendix E.

## Plots

Plots are a form of documentation as well as a method of presenting data. They indicate when calibrations were performed, when injections were made, and when the chamber is vented. They often indicate power failures, computer failures, or in general problems, and general quality of data.

### *Raw Data Plots ("P"- and "U"-file Plots)*

These are plots of raw uncorrected and at first unQAed data. "P"-file plots show raw "picked" (digitized data). "U" file plots show the raw DVM data, often including the AUTOCAL calibrations and venting. Both types of plots indicate completeness of data, ratios of conditions, profiles and general reasonableness of data. Discontinuities may indicate problems during picking.

### *Processed Data (G- and C-files QA plots)*

These plots of the final corrected data show immediately any problems or errors which might have occured in processing. Only valid experimental data should have been processed. Concentrations should be close to target conditions. Light, dew-point, and temperature data should be reasonable in magnitude.

### *Tracer Data Plots (CSTAR)*

Inert tracers are usually injected into each chamber half to monitor dilution during the experiment. Raw data are read and processed by a computer program CSTAR which fits the data to an exponential function with the least-squares method. The slope is the dilution rate which should be used by modelers. This data is processed for every run; chamber leaks can be detected quickly.

## Run Data Processing Status Databases

### *Description of Lab/Site Calenders*

Calendars have been discussed above. They are used as a primary documenting method. Experiments, calibrations, and some instrument or chamber work are indicated on the calendars at the site and the data processing office first. These are used to guide the data processing effort.

### *Description of* RUNENTRY *database*

A DATATRIEVE database maintained on the VAX is used to track all data processing and record the experimental conditions. The processing status of a single experiment or a group of experiments can be quickly assessed. It is used with report procedures to guide processing tasks. Tasks are listed by the priority given by a project coordinator.

The RUNENTRY system is a PL/I program that runs on the VAX-11/780 computer in the SPH. It provides on-line, interactive access to the database of run processing status. The program uses the VAX "electronic" Forms Management System to support a number of "forms" on a video display unit (terminal). The user can fill out the form, and the data are either called up from the database, or are stored in the database for future reference.

Table 16 is the individual record description for an entry in the database. In addition to the general information about the run conditions, the status of the processing steps for digital voltmeter data, for documentation preparation, for the processing of each instrument that had valid data, and for the progress toward creating the final file are stored in a record for each run.

There are a possible total of 110 checkpoint steps in processing a run. The events that are entered will be listed in sections following. The record provides for nine instruments, accounting for most of the checkpoints.

Single page printouts (132 columns wide) can be created for each run. An example of a printout is shown in Table 17. This shows a nearly completely processed run that had five instruments.

Figure 18, Figure 19, Figure 20, and Figure 21 are "hardcopies" of the terminal screen showing the "electronic" forms. These are designed to be used on terminal that have video attributes such as reverse fields (shown in the figures as dark areas), bold letters (not shown in figures), blinking areas and letters for attention. Each form also has on-line HELP for each field, and if more help is needed, the screens have full-screen help forms with such information as legal key values and HC species numbers.

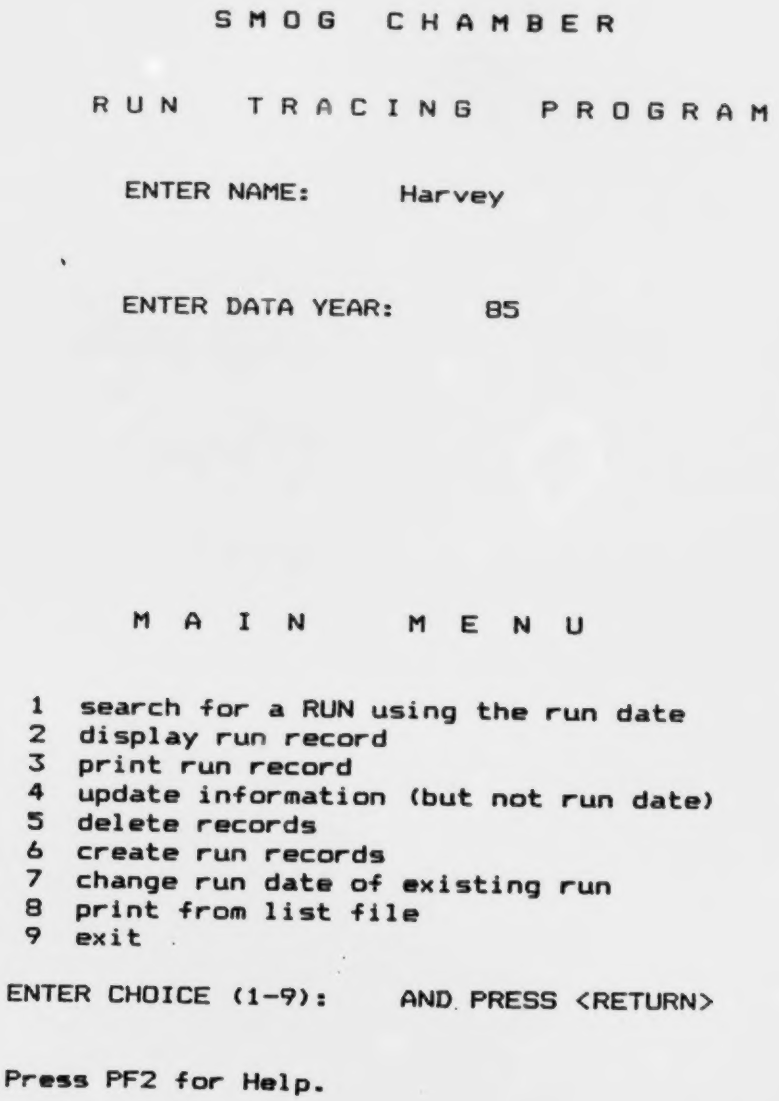
**Table 16.** Record Description for RUNENTRY Database System.

```
01 RUN_REC.
 02 GENERAL.
   03 RUN_DATE       USAGE IS DATE
      EDIT_STRING IS DD-MMM-YYYY.
   03 CONDITIONS     OCCURS 2 TIMES.
      06 SIDE        PIC X(4).
      06 NOXCONC     PIC 9.999.
      06 HC          OCCURS 3 TIMES.
         09 HCCONC     PIC 99.99
            MISSING VALUE IS 0.00
            EDIT_STRING IS  Z9.00?"     ".
         09 SPECIES  PIC 999.
   03 PROJECT        PIC X(4).
   03 QUALITY        PIC 9.
   03 PRIORITY       PIC 9.
 02 DETAIL.
   03 DVMDATA.
      06 ITEM        OCCURS 10 TIMES.
         09 DVEVENT    PIC X(3)
            DEFAULT IS "non"
            VALID IF DVEVENT IN DVEVENT_TAB.
         09 DVEDATE    USAGE IS DATE
            EDIT_STRING IS DD-MMM-YY.
         09 DVINIT     PIC X(3).
   03 DOCUMENTATION.
      06 ITEM        OCCURS 5 TIMES.
         09 DOEVENT    PIC X(3)
            DEFAULT IS "non"
            VALID IF DOEVENT IN DOEVENT_TAB.
         09 DOEDATE    USAGE IS DATE
            EDIT_STRING IS DD-MMM-YY.
         09 DOINIT     PIC X(3).
   03 FINAL_FILE.
      06 ITEM        OCCURS 5 TIMES.
         09 FFEVENT    PIC X(3)
            DEFAULT IS "non"
            VALID IF FFEVENT IN FFEVENT_TAB.
         09 FFDATE   USAGE IS DATE
            EDIT_STRING  IS DD-MMM-YY.
         09 FFINIT     PIC X(3).
   03 PICKDATA.
      06 TOTAL_SPECIES   PIC 99.
      06 NUM         PIC 9
         MISSING VALUE IS 0.
      06 INST        OCCURS 0 TO 9 TIMES DEPENDING ON NUM.
         09 ID       PIC X(3).
         09 ITEM     OCCURS 10 TIMES.
            11 PIEVENT PIC X(3)
               DEFAULT IS "non"
               VALID IF PIEVENT IN PIEVENT_TAB.
            11 PIDATE USAGE IS DATE
               EDIT_STRING IS DD-MMM-YY.
            11 PIINIT  PIC X(3).
```

## Table 17.

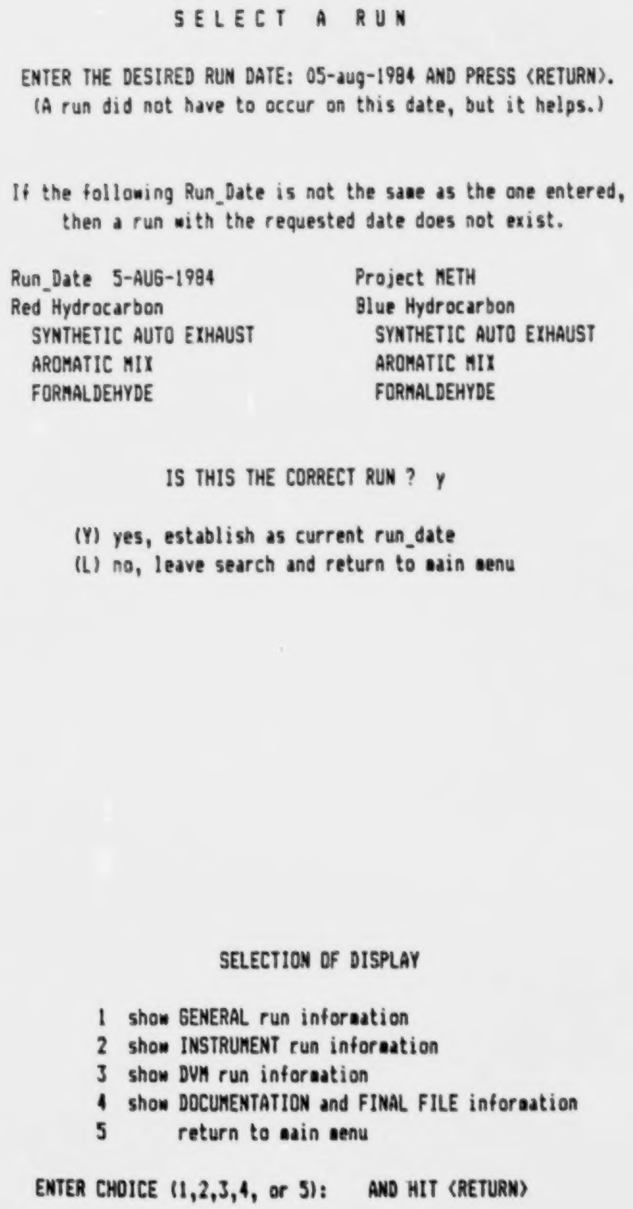
### RUNENTRY Processing Summary for September 14, 1081

```
                             Run Date: 14-SEP-1981    Project: REAC     Quality: 0    Priority: 9
SIDE   NOX      HCCONC   SPECIE  NAME
RED    0.300     2.60     191    Uncmix                           SIDE   NOX      HCCONC   SPECIE  NAME
                00.71     068    M-xylene                         BLUE   0.300     2.72     191    Uncmix
                00.00     000                                                      00.71    070    1,2,4-trimethylbenzene
                                                                                   00.00    000
--------COMPLETED DVM EVENTS--------
URU Unpack pgm run  12-OCT-1981 MOS    --------COMPLETED DOC EVENTS--------    ----COMPLETED FINAL FILE EVENTS-----
V2T AL tape created             MOS    SUM Run Sumry compl 29-OCT-1982 KGS     MRJ 3 sects merged   9-JAN-1983 HEJ
RPC Raw Plot creatd             RFP    D2V Doc tran to VAX  7-JAN-1983 KGS     U2T NL tape created 10-JAN-1983 HEJ
POA Plot QA compltd             KGS    V2T AL tape created  9-JAN-1983 RFP
CFS Cal facs determ 29-DEC-1981 KGS    T2D Tape trn to dsk  9-JAN-1983 HEJ
DRU DVMFIX pgm run   7-JAN-1983 RFP    DOA Doc QA completd  9-JAN-1983 HEJ
COA Conc QA compltd  7-JAN-1983 KGS
R2M Ready to merge   9-JAN-1983 HEJ

----COMPLETED INSTRUMENT EVENTS-----    ----COMPLETED INSTRUMENT EVENTS-----   ----COMPLETED INSTRUMENT EVENTS-----
Instrument:  C1G Carle I GC             Instrument:  C2G Carle II GC           Instrument:  FOG CEA Formaldehyde
PID Pick instrc det 18-MAY-1982 KGS     PID Pick instrc det 18-MAY-1982 KGS    PID Pick instrc det 18-MAY-1982 KGS
PRU PICK pgm run    27-OCT-1982 JLH     PRU PICK pgm run     5-APR-1982 JLH    PRU PICK pgm run     7-APR-1982 JLH
FPT Fast plot creat 27-OCT-1982 JLH     FPT Fast plot creat  5-APR-1982 JLH    FPT Fast plot creat  7-APR-1982 JLH
POA Fst plt QA comp 28-OCT-1982 KGS     POA Fst plt QA comp 28-OCT-1982 KGS    POA Fst plt QA comp              KGS
CFD Cal facs determ 25-MAY-1982 KGS     CFD Cal facs determ 25-MAY-1982 KGS    CFD Cal facs determ  1-JUL-1982 KGS
CRU CALCON pgm run  27-OCT-1982 JLH     CRU CALCON pgm run   8-SEP-1982 CDM    CRU CALCON pgm run   8-SEP-1982 KGS
HRU HCANAL pgm run  27-OCT-1982 JLH     HRU HCANAL pgm run   8-SEP-1982 CDM    COA Comp Chksht QA  28-OCT-1982 KGS
COA Comp Chksht QA  27-OCT-1982 KGS     COA Comp Chksht QA  28-OCT-1992 KGS    F2V Files tr to VAX  7-JAN-1983 RFP
F2V Files tr to VAX  7-JAN-1983 RFP     F2V Files tr to VAX  7-JAN-1983 RFP    V2U Ready to merge   9-JAN-1983 HEJ
V2U Ready to merge   9-JAN-1983 HEJ     V2U Ready to merge   9-JAN-1983 HEJ
                                                                               ----COMPLETED INSTRUMENT EVENTS-----
----COMPLETED INSTRUMENT EVENTS-----    ----COMPLETED INSTRUMENT EVENTS-----
Instrument:  V2G Varian GC (gas)        Instrument:  COG Beckman 6800 (CO)
PID Pick instrc det 18-MAY-1982 KGS     BAD Stop processing 18-MAY-1982 KGS
PRU PICK pgm run     7-APR-1982 JLH
FPT Fast plot creat  7-APR-1982 JLH
POA Fst plt QA comp             KGS
CFD Cal facs determ 21-MAY-1982 KGS
CRU CALCON pgm run  15-OCT-1982 JLH
COA Comp Chksht QA  28-OCT-1982 KGS
F2V Files tr to VAX  7-JAN-1983 RFP
V2U Ready to merge   9-JAN-1983 HEJ
```



```
          S M O G   C H A M B E R

     R U N   T R A C I N G   P R O G R A M

        ENTER NAME:      Harvey


        ENTER DATA YEAR:      85




            M A I N    M E N U

  1  search for a RUN using the run date
  2  display run record
  3  print run record
  4  update information (but not run date)
  5  delete records
  6  create run records
  7  change run date of existing run
  8  print from list file
  9  exit

  ENTER CHOICE (1-9):     AND PRESS <RETURN>

  Press PF2 for Help.
```

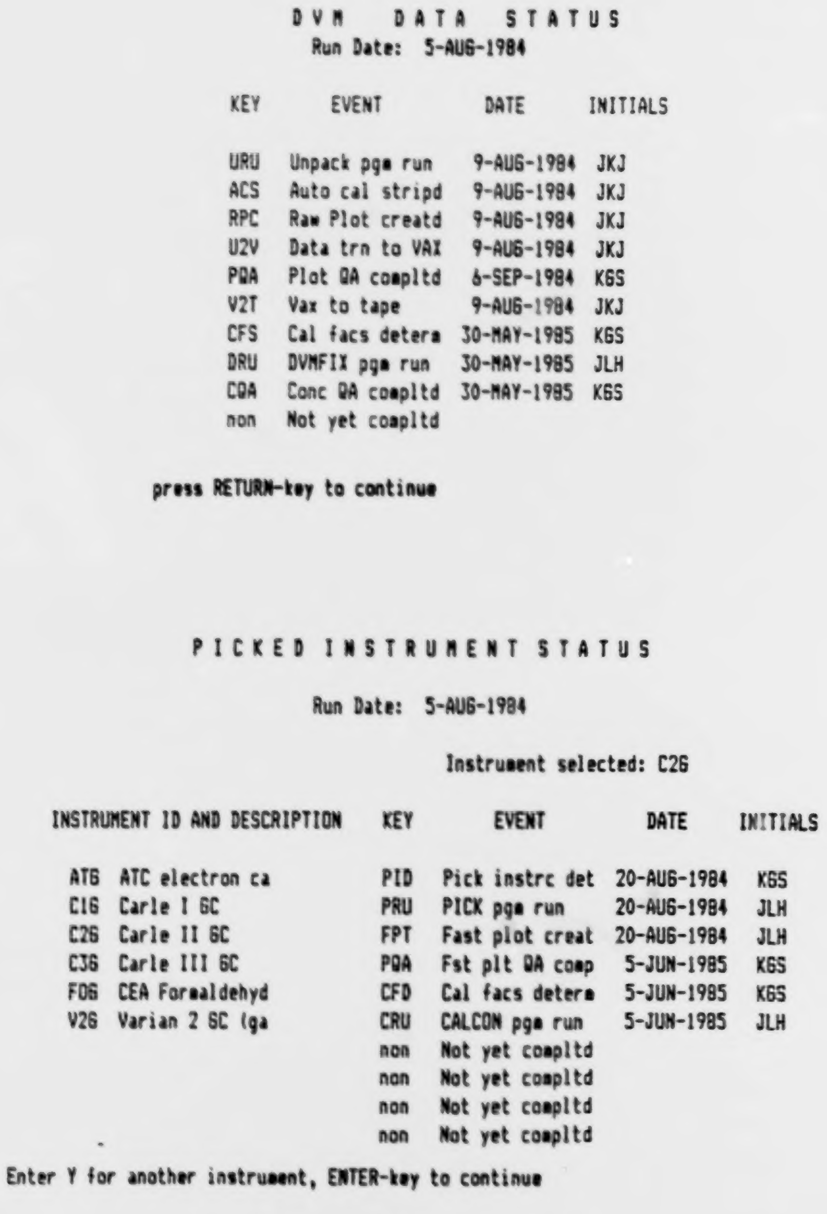
Figure 18. Runentry Welcome and Main Menu Screens



```
                    S E L E C T   A   R U N

     ENTER THE DESIRED RUN DATE: 05-aug-1984 AND PRESS <RETURN>.
      (A run did not have to occur on this date, but it helps.)


   If the following Run_Date is not the same as the one entered,
       then a run with the requested date does not exist.

   Run_Date  5-AUG-1984              Project METH
   Red Hydrocarbon                   Blue Hydrocarbon
     SYNTHETIC AUTO EXHAUST            SYNTHETIC AUTO EXHAUST
     AROMATIC MIX                      AROMATIC MIX
     FORMALDEHYDE                      FORMALDEHYDE

                   IS THIS THE CORRECT RUN ?  y

         (Y) yes, establish as current run_date
         (L) no, leave search and return to main menu
```

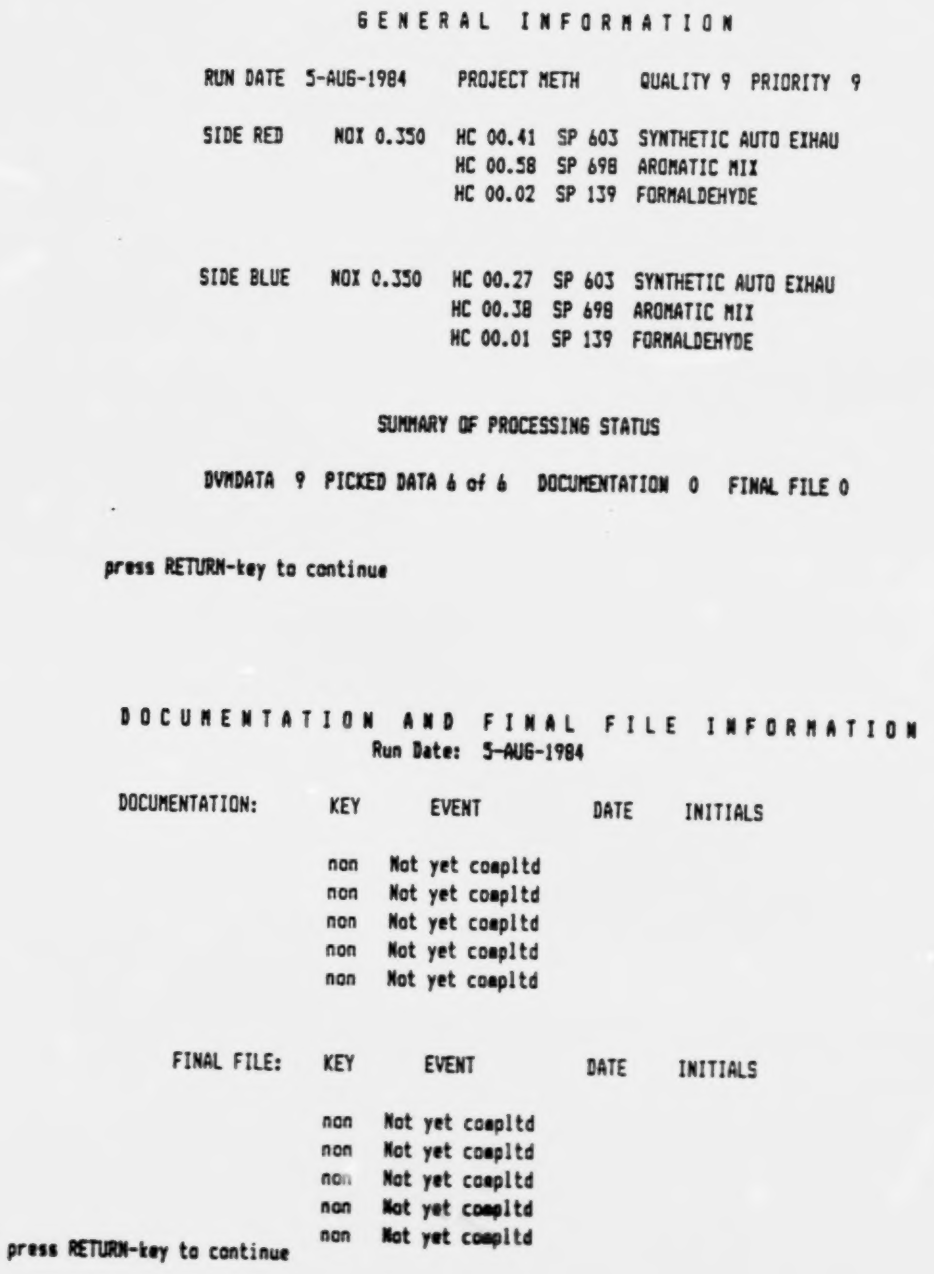
```
                        SELECTION OF DISPLAY

              1  show GENERAL run information
              2  show INSTRUMENT run information
              3  show DVM run information
              4  show DOCUMENTATION and FINAL FILE information
              5       return to main menu

     ENTER CHOICE (1,2,3,4, or 5):    AND HIT <RETURN>
```

**Figure 19.** RUNENTRY Date and Display Selection Screens



```
                    D V M    D A T A    S T A T U S
                      Run Date:  5-AUG-1984

               KEY       EVENT           DATE       INITIALS

               URU   Unpack pgm run     9-AUG-1984   JKJ
               ACS   Auto cal stripd    9-AUG-1984   JKJ
               RPC   Raw Plot creatd    9-AUG-1984   JKJ
               U2V   Data trn to VAX    9-AUG-1984   JKJ
               PQA   Plot QA compltd    6-SEP-1984   KGS
               V2T   Vax to tape        9-AUG-1984   JKJ
               CFS   Cal facs determ   30-MAY-1985   KGS
               DRU   DVMFIX pgm run    30-MAY-1985   JLH
               CQA   Conc QA compltd   30-MAY-1985   KGS
               non   Not yet compltd

        press RETURN-key to continue



                P I C K E D   I N S T R U M E N T   S T A T U S

                             Run Date:  5-AUG-1984

                                          Instrument selected: C2G

     INSTRUMENT ID AND DESCRIPTION    KEY        EVENT          DATE      INITIALS

       ATG  ATC electron ca           PID   Pick instrc det  20-AUG-1984    KGS
       C1G  Carle I GC                PRU   PICK pgm run     20-AUG-1984    JLH
       C2G  Carle II GC               FPT   Fast plot creat  20-AUG-1984    JLH
       C3G  Carle III GC              PQA   Fst plt QA comp   5-JUN-1985    KGS
       FOG  CEA Formaldehyd           CFD   Cal facs determ   5-JUN-1985    KGS
       V2G  Varian 2 GC (ga           CRU   CALCON pgm run    5-JUN-1985    JLH
                                      non   Not yet compltd
                                      non   Not yet compltd
                                      non   Not yet compltd
                                      non   Not yet compltd

    Enter Y for another instrument, ENTER-key to continue
```

Figure 20. RUNENTRY General, Documentation, and File Status Screens



```
                      G E N E R A L   I N F O R M A T I O N

            RUN DATE  5-AUG-1984     PROJECT METH      QUALITY 9  PRIORITY  9

            SIDE RED     NOX 0.350   HC 00.41  SP 603  SYNTHETIC AUTO EXHAU
                                     HC 00.58  SP 698  AROMATIC MIX
                                     HC 00.02  SP 139  FORMALDEHYDE


            SIDE BLUE    NOX 0.350   HC 00.27  SP 603  SYNTHETIC AUTO EXHAU
                                     HC 00.38  SP 698  AROMATIC MIX
                                     HC 00.01  SP 139  FORMALDEHYDE

                             SUMMARY OF PROCESSING STATUS

            DVMDATA  9  PICKED DATA 6 of 6   DOCUMENTATION  0   FINAL FILE 0


       press RETURN-key to continue



    D O C U M E N T A T I O N   A N D   F I N A L   F I L E   I N F O R M A T I O N
                              Run Date:  5-AUG-1984

    DOCUMENTATION:       KEY       EVENT           DATE     INITIALS

                         non   Not yet compltd
                         non   Not yet compltd
                         non   Not yet compltd
                         non   Not yet compltd
                         non   Not yet compltd

           FINAL FILE:   KEY       EVENT           DATE     INITIALS

                         non   Not yet compltd
                         non   Not yet compltd
                         non   Not yet compltd
                         non   Not yet compltd
press RETURN-key to continue  non   Not yet compltd
```

**Figure 21.** RUNENTRY DVM and Picked Instrument Status Screens

Several report procedures have been developed to help guide the data processing. These look up the status in `RUNENTRY` for specific tasks for each "type" of personnel: `PCREPORTS`, `PPREPORTS`, `CTREPORTS`. These were explained in Chapter 2. An example of the `PCREPORT` is shown in Figure 22.

Figure 22. PCreport Example

```
Count of runs that have reached stated stages of processing
           for ALLRUN84
Total runs Total Inst
    63        312
******** DVM data ************
URU RPC ACS NAC U2V V2T PQA CFS DRU CQA R2M NTB BAD NDV
 58  58  58   0  57  57  54  38  37  37   0   2   1   3
     Sum of URU, NTB, and NDV is   63
######## Inst data ############
PID PRU FPT PQA CFD CRU HRU CQA F2V V2U NTB BAD
190 190 190 116 104 104   0  17   0   0 135   6
     Sum of PID and NTB is  325
######## Documentation ############
SUM D2V DQA
  7   7   2
######## Final File ############
MR3 ALT FQA
  0   0   0
Number of P-files should be : 190
Number of C-files should be : 104
Number of K-files should be : 104
```

**Figure 22(cont.). PCreport Example**

```
ALLR runs/instuments needing Picking Instructions Determined (PID).
     This is an INST first processing stage report.
------------------------------------------------------------
                     PRIORITY >>> 8 <<<
         26-Jun-84  Number of inst =   8
              PCG  PE 900 GC
                   (chamber)
------------------------------------------------------------
                     PRIORITY >>> 5 <<<
         25-Jun-84  Number of inst =   8
              PCG  PE 900 GC
                   (chamber)
    ALLR runs/instuments needing Cal Factors Determined (CFD).
   The following instruments have ( PID ) Pick inst det completed
                          but not ( CFD ) Cal fac det completed.
           RUN
           DATE        Instruments              Date done     Person
------------------------------------------------------------
                     PRIORITY >>> 9 <<<
         25-Jul-84  Number of inst =   5
              V2G  Varian GC (gas)
                    PID    Pick inst det         6-Aug-84      KGS
------------------------------------------------------------
                     PRIORITY >>> 5 <<<
         25-Jun-84  Number of inst =   8
              COG  Beckman 6800 (CO)
                    PID    Pick inst det        31-Jul-84      JA
              V2G  Varian GC (gas)
                    PID    Pick inst det        31-Jul-84      JA
```

## Description of Data Processing Status Database

This section describes the data processing status database and how it is used.

### Description

The main parts of the data processing status database are the calendars and the `RUNENTRY` `DATATRIEVE` system. `RUNENTRY` maintains status information for each experiment by date. The general categories are:

- GENERAL
  - experimental chemical conditions for both sides,
  - quality and priority index,
  - number of experiments
- INSTRUMENT
  - pick instructions,
  - cal factors given,
  - QA performed,
  - final processing steps performed;
- DVM
  - unpacking performed,
  - cal factors given,
  - QA steps performed,
  - final processing performed;
- DOCUMENTATION
  - final documentation processed and written,
  - moved to VAX for final segfile formation.

### Use of Data Processing Status Database

This section describes how the database is used from the time the experiment is conducted to final processing.

#### *Log Experiment*

When an experiment is conducted (attempted), the conditions and general quality are indicated on both calendars (site and office). This information is usually obtained by telephone conversations between the project coordinators and site personnel within a few hours after the start of the experiment in order to plan for the next days activities. Another late afternoon telephone conversation follows to determine the outcome of the experiment and to finalize the next days plans. If the experiment is thought to be successful or might provide any the useful information, it is considered to exist. The absence of major negative comments such as "failure" written on the calendar, triggers the data processing procedure. The experiment is packed-up and inventoried if it is not considered a "failure" for transport to the dataprocessing office.

From the telephone conversation mentioned above, the experiments success is determined. If the experiment is considered worth archiving, the actual experiment conditions and general quality are recorded on the calendars. Otherwise the attempted experiment and the problems associated are noted on the calendar.

Data processing personel expect both the runfolder and data floppies to be transported to the school within a few days after the experiment. Special locations in the office are set aside for incoming data. The calendars and these areas are checked daily. If data is late, the site personel are contacted and questioned. When either the run folder or data floppies arrive at the office, the experiment is entered into the RUNENTRY database.

The contents of the runfolder are first inventoried before any data processing occurs. The instrument checklist completed during the experiment is compared with the folder contents. Missing items are investigated.

### *Preliminary Review*

Preliminary review usually begins the day or day after an experiment is conducted by a PC. Conversations with the site operators indicate resulting experimental conditions and outcome and any problems which might have occured. The run folder contents are inspected. Instrument operation behavior, chamber background(proper venting, drying or absence of condensation), temperature and dewpoint, sunlight, initial conditions, and reasonableness of results are determined. Basic quality and processing priority is determined. Completeness for data and documentation is determined. The calendars and the RUNENTRY database are updated. Besides a QA step for the experiment itself, the success of meeting the experimental plan goals is checked. A variation in the experiment might be useful if documented but would result in rescheduling of the target experiment.

### *Processing Instructions and Information*

RUNENTRY is used to track data processing by recording of processing events. Automatic status reports can be generated. Report procedures are used to guide and assign processing tasks: **PCREPORTS**, **PPREPORTS**, and **CTREPORTS**. The reports are listed by priority (0-9) as determined by the **PC**.

**PCREPORTS** tells the project coordinators that picking instructions are needed, or picked data exists and needs QA and calibration factors, or final data exists and needs QA. **CTREPORTS** indicates to the computer technicians that **DVM** data needs unpacking and archival, and **AUTOCAL** data needs to be stripped. **PPREPORTS** tells the peakpickers that pick instructions have been given, or that picked data has bee QAed and calibration factors exist for final processing.

Each worker updates **RUNENTRY** as each step is performed. The presence of each new step completed generates instructions to the next appropriate worker to perform the next processing task when a new report is generated. When all processing steps are completed, the segmented file is assembled, and the final initial experimental conditions and quality are updated in the **RUNENTRY** GENERAL section. This data is input to the **RUNSUMMARY** database which is used to sort, organize, and analyze the total smog chamber experimental database.

## Digital Voltmeter Data Processing

The Digital Voltmeter Data (**DVM**) from the Computer **DA** system is usually processed easily once the calibration database is established. The processing flowchart is indicated in Figure 23. The **RUNENTRY** events flowchart is shown in Table 18.

The computer technician (CT) "unpacks" the data from the two floppies which arrive from the research site. Several files generated by the site **DA** system are copied to the **LSI-11** harddisk: the main **DVM** file (**mmddy.DVM**), the remarks file (**mmddy.REM**), the command file (**mmddy.CMD**), the adjustments file (**mmddy.ADJ**), and the file of actual computer commands (**mmddy.OPS**). Printouts of all of these files except the **mmddy.DVM** file are made and stored in the **RUNFOLDER**. A computer program (**UNPACK**) is run which produces a "U" file, which is the same raw data but in ASCII format and is the principle raw data file for the smog chamber experiment. This file contains 24 hours of data taken every minute for every instrument connected to the **DVM**. The "U" file is back-up onto two sets of floppies, and to two types of magnetic tape used on different computers: the **VAX-780** and the University's **IBM 4381**.

Several programs are used to process data from the "U-file". **FASTDV** is run several times: to produce "P" files for plotting the raw data ("fastplots") from the experiment and to strip the **AUTOCAL** data (makes "A" file). The processing of the calibration data was discussed earlier. **PLOPIC** is used to make the plots from the "P" files for the $NO_x/O_3$ plot and the TSR/UV, temperature, and dewpoint plot. Theses plots are stored both in the **RUNFOLDER** and the **FASTDV** notebook. All of the

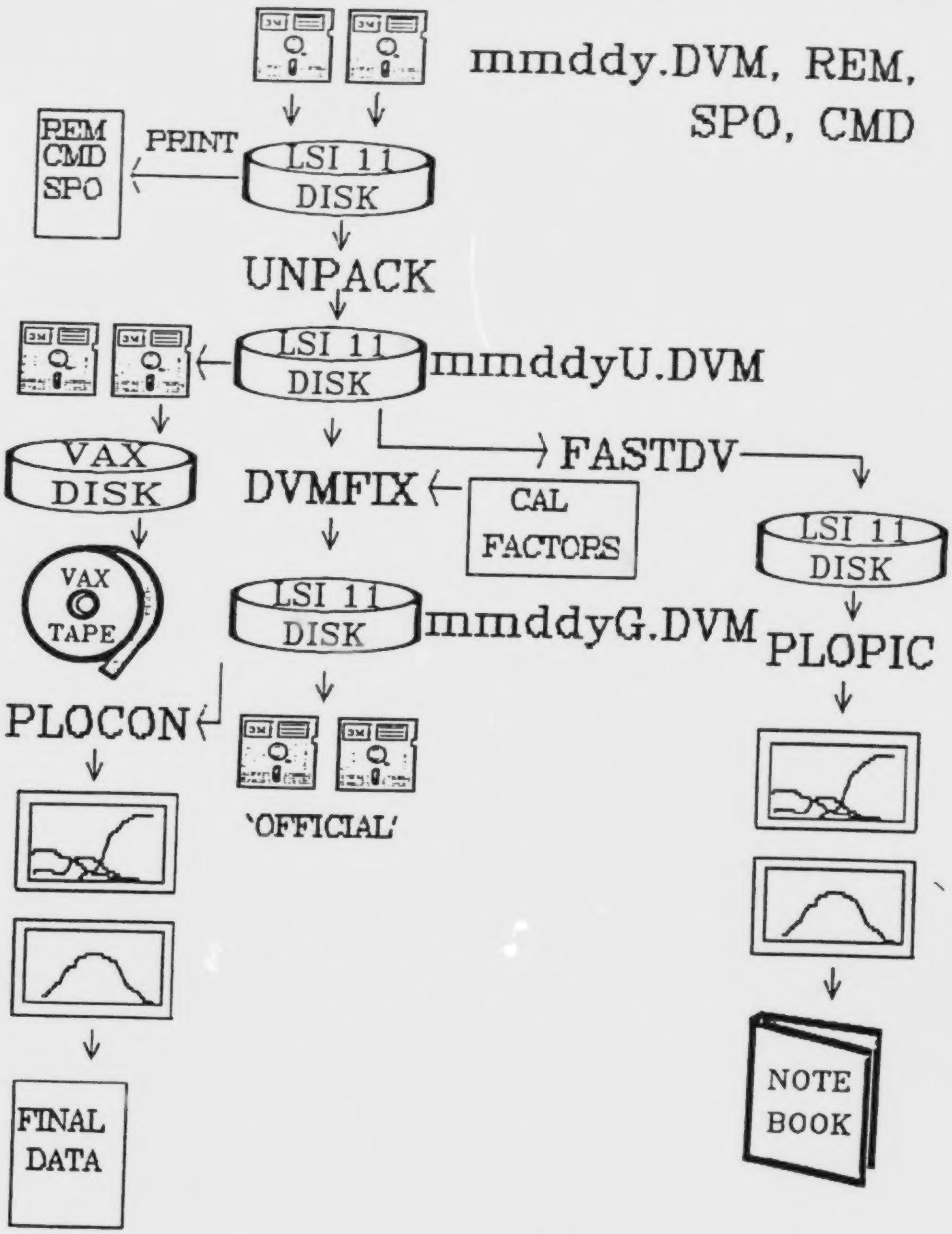

mmddy.DVM, REM,
SPO, CMD
REM
CMD
SPO
PRINT
LSI 11
DISK
UNPACK
LSI 11
DISK
mmddyU.DVM
VAX
DISK
VAX
TAPE
FASTDV
DVMFIX
CAL
FACTORS
LSI 11
DISK
LSI 11
DISK
mmddyG.DVM
PLOPIC
PLOCON
'OFFICIAL'
FINAL
DATA
NOTE
BOOK

Figure 23. DVM Processing Flowchart (Computers and Files)

## Table 18.

### Processing System for DVM Data

```
 cal processing
 /             \
tot runs       (CFS)-------
 \             /            \
  \       (ACS)              \
   \     /                    \
   (URU)------(RPC)----!PQA!-<DRU>--!CQA!--!R2M!
        \                     /
         (UTV)               /
              \             /
               (V2T)-------
```

```
!sss! == stages determined by Project coordinator (PC)
<sss> == stages determined by Peak Pickers (PP)
(sss) == stages determined by Computer Techs (CT)
```

DVM data processing steps

| Pers | Step | Meaning |
|---|---|---|
| CT | URU : Unpack run | Site floppy data expanded to ASCII |
| CT | U2V : Data to VAX | Ufiles moved from LSI disk to VAX |
| CT | V2T : to archive tape | Data moved from VAX to tape |
| CT | RPC : Raw Plot done | Plot of voltages to examine data |
| PC | PQA : Plot QA | Initial quality check |
| CT | ACS : AutoCals strip | Cals separated for processing |
| PC | CFS : Cals done | Calibration factors determined |
| CT | DRU : DVMFIX run | Voltages changed to concentrations |
| PC | CQA : Conc QA | Concentration Quality Assurance |
| CT | R2M : Ready 2 merge | Merge process on VAX can be run |
| PC | NTB : Not to be proc | Not to be processed |
| PC | BAD : Stop processing | Something is wrong with this data |
| CT | NDV : No DVM data | |

tasks discussed so far are done by the CT. The CT update RUNENTRY as these tasks are performed.

When the FASTDV plots are made and RUNENTRY has been updated so, the PCREPORT will direct the PC to perform a QA on the raw data. The plot is compared with the original stripcharts. If data is missing, the documentation (RUNSHEETS, REMARKS FILES, INSTRUMENT CHECKLIST, CALENDARS) is investigated for mention of power or computer failures, or instrument malfunction. The data may need to be retransfered from the site. Missing data may have to digitized from the stripcharts. Once the raw data is QAed, the PC updates RUNENTRY that the raw data has been unpacked successfully (PQA) and calibration factors can be applied (calibration factors need to be determined).

Calibration factors are applied to raw DVM data with a program called DVMFIX which runs on the LSI computer. The program also controls which time periods of raw data are processed. Bad data, or cal data is eliminated in this way. Calibration factors are obtained from a list resulting from calibration factor processing discussed above. Interpolation may be required. Usually however $NO_x$ and $O_3$ monitors are calibrated twice a day, before and after each experiment. The calibration factors can be used directly.

The PC fills out a DVMFIX sheet indicating the calibration factors to apply to the data, the periods of valid data to process, and brief documentation. The calibration factors are obtained from the AUTOCAL report as described above. The PC updates RUNENTRY that calibration factors have been determined. The information on the DVMFIX sheet is transfered to a file on the LSI-11 computer (mmddy.CRD) usually by a PP or CT. The "U" file is moved back to the harddisk. This might require the assistance of the CT if these files are not still on floppies and need to be copied off of one of the magnetic tapes. The program DVMFIX is used to apply the calibration data in the mmddy.CRD file to the raw data, producing a new file of corrected data for only valid experimental data for every fourth minute (mmddyG.DVM "G-file"). DVMFIX is usally run by the person who creates the mmddy.CRD file. The "G-files" are backed-up on floppies. RUNENTRY is updated that DVMFIX has been run and final QA is need by the PC.

The final corrected data is listed and plotted. Concentration data for NO and $NO_2$ must equal $NO_x$ concentrations within a few ppb throughout the experiment. "Zeros" are checked. Initial conditions are compared with the target conditions. Dewpoint, and temperature data are checked for consistency and reasonableness (dewpoint data cannot be higher than chamber temperature). Profiles and maximum values of light are compared with other seasons for resonableness. Data not to be processed or missing should have "-9.9999" indicated. If there are problems, the PC will re-issue processing instructions, deleting from RUNENTRY that DVMFIX has been run. This will cause the PPREPORTS and CTREPORTS to request that the data be reprocessed. The process is repeated until the QA criteria are satisfied.

## Strip Chart Data Processing

Processing strip chart data is a little more complex than processing DVM data. More data is represented, more calibration factors are required, and there are more sources of error. Basically the data are identified, the conditions of the instruments are identified, the data is picked (digitized), plotted, and QAed, calibration factors are determined and applied, and the final data is listed and plotted for final QA. The processing flowchart is indicated in Figure 24. The RUNENTRY events flowchart is shown in Table 19.

Data processing starts with RUNENTRY indicating to the PC in the PCREPORT that pick instructions are needed for the instruments used in an experiment. Data processing starts with the documentation. The RUNSHEET and RUNENTRY indicate which species where injected for the experiment. The instruments which require processing are identified. The stripcharts are investigated for proper documentation: attenuation, chart full scale setting and chart speed, time, and chamber side sampled. The chromatograms are inspected for proper appearance (operation). The background chromatograms are inspected for contamination. Major problems are noted. If the data is valid but not useful the NTB is indicated in RUNENTRY. If the data is bad, BAD is indicated. No further action will be taken.

If the instrument seems to be free of problems and data are considered useful, then pick instructions are given. Calibration data are identified and noted as not to be processed by the peakpicker (PP). The compounds monitored and their peaks are identified and labeled. The entire stripchart is inspected for reasonable appearance and operation and data. Problems are identified and noted. The peakpicker can indicate in the data that data are missing (off-scale, power failure, instrument adjustment, *etc.*). The start and end times of valid data are identified. The compounds to be picked are listed on the DATA PROCESSING INSTRUCTION FORM with any additional instructions. RUNENTRY is updated with PID (pick instructions determined) by the PC. This indicates in the PPCREPORT to the PP that data is ready to be picked.

The PP obtains the run folder and determines from the DATA PROCESSING INSTRUCTION FORM which compounds are to be picked. The stripchart is removed and spread out over the digitizer pad. Using the instructions and peak identification on the stripchart the data is digitized using the program DIGPIK run on the LSI-11 computer to produce a file named mmddyP.iit ("P" file). The files are backed-up on floppies and magnetic tape. The data is then plotted with a program called PLOPIC on the LSI-11 with GIGI graphics. A hardcopy is stored in the RUNFOLDER. The PP

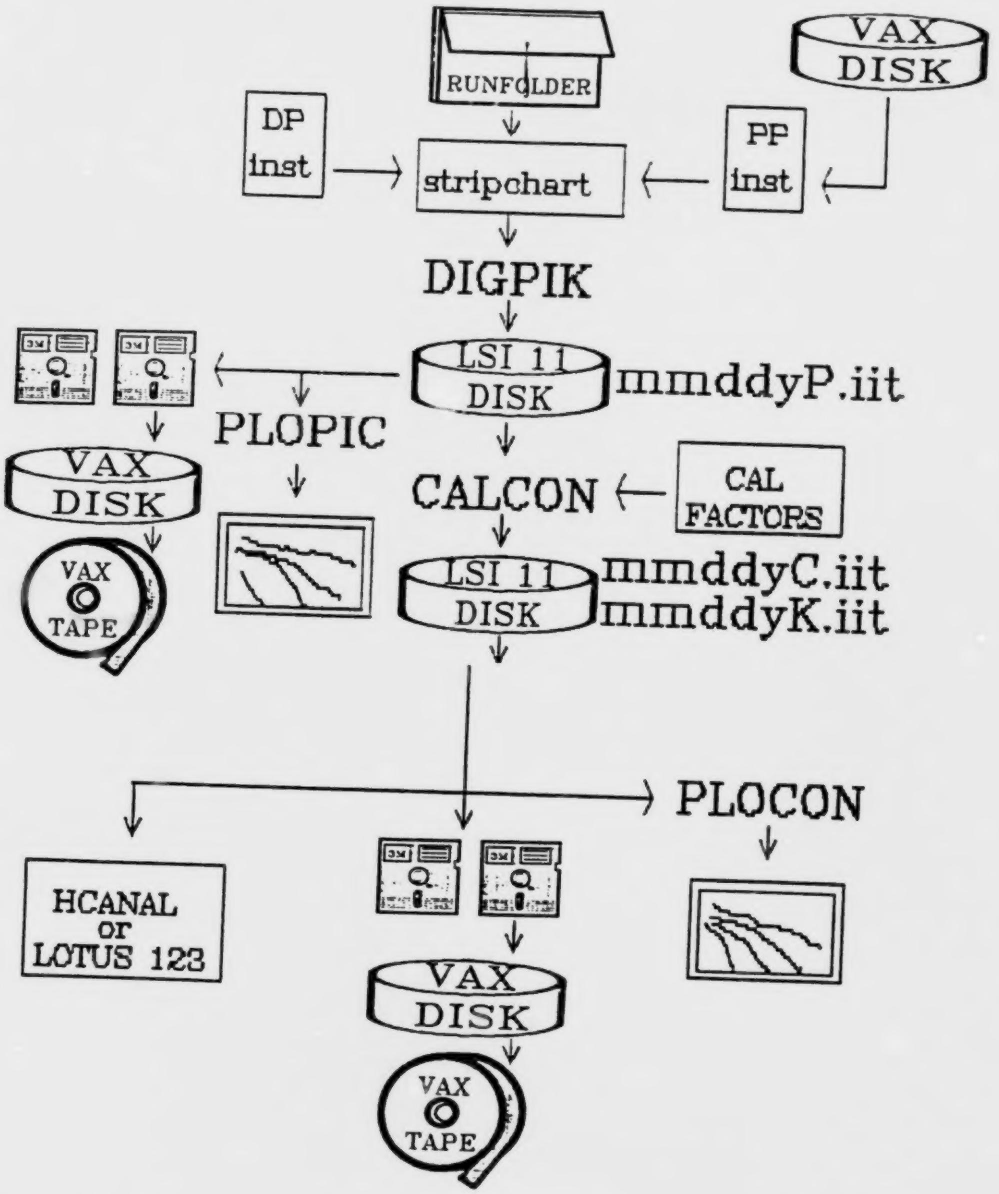

RUNFOLDER
VAX DISK
DP inst
stripchart
PP inst
DIGPIK
LSI 11 DISK
mmddyP.iit
PLOPIC
VAX DISK
VAX TAPE
CALCON
CAL FACTORS
LSI 11 DISK
mmddyC.iit
mmddyK.iit
PLOCON
HCANAL or LOTUS 123
VAX DISK
VAX TAPE

**Figure 24.** Instrument Processing Flowchart (Computers and Files)

## Table 19.
## Processing System for Instrument Data

```
    !NTB!
   /
tot inst  __ cal processing_
   \     /                  \
    !PID!                    !CFD!       <HRU>__
        \                        \     /        \
         \                        <CRU> -------- !CQA!---- (F2V)
          \                      /
          <PRU>---- <FPT> --!PQA!

          !sss! == stages determined by Project coordinator (PC)
          <sss> == stages determined by Peak Pickers (PP)
          (sss) == stages determined by Computer Techs (CT)
```

| Pers | RUNENTRY stages | Meaning |
|---|---|---|
| ---- | --------------------- | ------------------------------------ |
| PC | PID : Pick inst det | Charts marked, Inst status sheet |
| PC | NTB : Not to be proc | No futher processing marked on Inst sheet |
| PC | CFD : Cal fac det | Cal factors for each comp entered on status sheet in folder |
| PP | PRU : Pick run | Data has been digitized and P-file |
| PP | FPT : FPlot done | P-file has been plotted |
| PC | PQA : FPlot QA | Fast plot has been marked OK (no bad points in P-file) |
| PP | CRU : CALCON run | C and K files exist on floppies |
| PP | HRU : HCANAL run | HC analysis printout in run folder |
| PC | CQA : Comp CS QA | Instrument QA completed<br>Initial Conditions updated |
| CT | F2V : File 2 VAX | C and K files moved to VAX |
| CT | V2U : Ready 2 merge | C files merged together, K files together |
| PC | BAD : Stop processing | Something is wrong with this data |

updates RUNENTRY that the data has been picked (PRU: pick run) and a "fastplot" has been made (FPT). This indicates in the PCREPORT to the PC that raw data has been picked and requires QA.

The "fastplot" is inspected and compared with the original stripchart. Appropriate chemical behavior is noted. The stripchart data is compared to assure that the data is picked correctly: time and side for chromatograms and amplitude of peaks. When possible, picked data is inspected for consistency: similar compounds on the different sides should show similar behavior, and the least reactive side should match the picked data side indicating less or less reactive material. If additional or correctional picking is required, the PC deletes the PRU and FPT entries, and changes the date for the PID instructions to the current date. This will indicate to the PP that picking is required. Comments on the DATA PROCESSING INSTRUCTION FORM will indicate the new work required with notes added by the PC during the last QA procedure. Once the correction PP work is performed, RUNENTRY will be updated with PRU again which will indicate raw data QA procedures are needed again to the PC in the next PCREPORT. If the data passes the QA tests, the PC enters PQA to RUNENTRY which will indicate to the PC in future PCREPORTs that calibration factors are needed for further data processing.

Once the picked data is QAed, calibration factors need to be determined for final data processing: conversion of raw picked data ("P files") to concentration data ("C" files). The techniques for determining appropriate calibration factors was discussed above. The calibration factors are indicated on the DATA PROCESSING INSTRUCTION FORM. The PC indicates that calibration factors have been determined by entering into RUNENTRY CFD (calibration factors determined). This will indicate to the PP that raw data is ready to be converted to concentration data in the next, PPREPORT.

A program (CALCON) which runs on the LSI-11 computer is used to apply the calibration factors to the raw data ("P"-files), and to document which factors were used, who determined them, who is running the program and when, the full names of the compounds (abbreviations are used to identify data fields), and the maximum amplitudes of the raw and final concentration data. Two separate files are produced, the actual concentration data (`mmddyC.iit`, "C" file) and the documentation (`mmddyK.iit`, "K" file). The resulting files are listed, and the data is plotted for final QA with PLOCON, a plotting program using GIGI graphics and the LSI-11. These are retained in the run folder. The PP indicates that the CALCON program was run by entering CRU. This will indicate to the PC that concentration files are ready for final QA in the next PCREPORT.

The QA procedure for the final concentration data varies with the complexity of the experiment and the chemical species. The first checks however are to look at the documentation file ("K" file) and the `DATA PROCESSING INSTRUCTION FORM` to be sure that the desired calibration factor(s) was actually applied. The `PLOCON` plot is inspected to determine if the resulting data is reasonable and consistent with the other experimental data and the indicated target conditions on the `RUN SHEET`. If the concentrations of the initial conditions are far from the target conditions, a reasonable explanation must be found. Often the `RUN SHEET`, `REMARKS FILE` printout, or the `INSTRUMENT CHECKLIST` will indicate problems which could explain the discrepancies. Usually resulting data is not more than 25 percent from the target conditions.

If the concentration data is for a standard HC mixture, a compositional analysis should conform well with the known composition. An option of the `CALCON` program is to produce files which are readable by a computer program (`HCANAL`) for compositional analysis. In some cases where several experiments are performed with a similar mixture, the concentration data for the initial conditions for all the experiments are entered into a `LOTUS` spreadsheet for relational composition analysis. Calibration factors should result in data which when analyzed yields a consistent composition if indeed a similar mixture was used throughout the program. QA procedures may indicate that the calibration factors are not reasonable or that the raw data is invalid. See the discussion above for determination of calibration factors. Invalid data may require special processing, or a decision that the data is not processable (`BAD`). Once QA procedures are successfully performed, `RUNENTRY` is updated with `CQA` (concentration data QA performed). The "C" and "K" files are backed-up on floppies. If new factors are needed, the `CRU` is deleted and the `CFD` date is updated. New factors are indicated with explanations on the `DATA PROCESSING FORM`.

Once the final QA procedures are completed, the "C" and "K" files are transfered from the `LSI-11` to the `VAX` (`RUNENTRY F2V`) to await merging with the `DVM` data and the documentation, to form the final segmented data file for distribution. The "P", "C", and "K" files are backed up on `VAX` magnetic tape. The `RUN_CAL_USED` database is updated with the calibration factors used in data processing. Initial conditions are updated in `RUNENTRY` in the general section and `RUNSUMMARY`.

## Documentation Processing

Documentation is associated with all phases of the experiment; recorded on many sources. Much is needed only to process the data. Some documentation data however is processed to be included with the final data files. Calibration factor documentation is processed as the data is processed ("K" file, see discussion above). Some other documentation however is needed, which increases the value of the resulting final data.

A general documentation file is produced in addition to the concentraion data files (`mmddyy.DOC`). It becomes the first part of the final segmented data file. Its purpose is to convey all information with the data file itself, required to describe the experiment, and data which might be useful to photochemical modelers. The processing flowchart is indicated in Figure 25. The `RUNENTRY` events flowchart is shown in Table 20.

20

**Documentation Steps**

```
                 DOCUMENTATION data processing steps
Pers     Step                   Meaning
----     --------------------   ------------------------------------
PC       SUM : Run sum done     DVM, Instrument, and Raw Quality
CT       D2V : Doc  to VAX      Documentation transferred to VAX
PC       DQA : Doc QA           Documentation Quality Assurance
```

### General Documentation Form

A five page paper form called `General Documentation` is used throughout all stages of the data processing. All documentation needed to be included in the final general documentation file is recorded on this form as data are processed. In addition the form includes checklists and formulas used to arrive at a general quality index that is specified in the final documentation file. An example form is included in Appendix E.

### General Description and Purpose of Experiment

The first part of the general documentation file is the experimental run date which is the primary identifier of an experiment. A general description of the experiment follows. The purpose of the experiment is included if it is not clear from the description. Results are sometimes added if a specific comparison was being made.

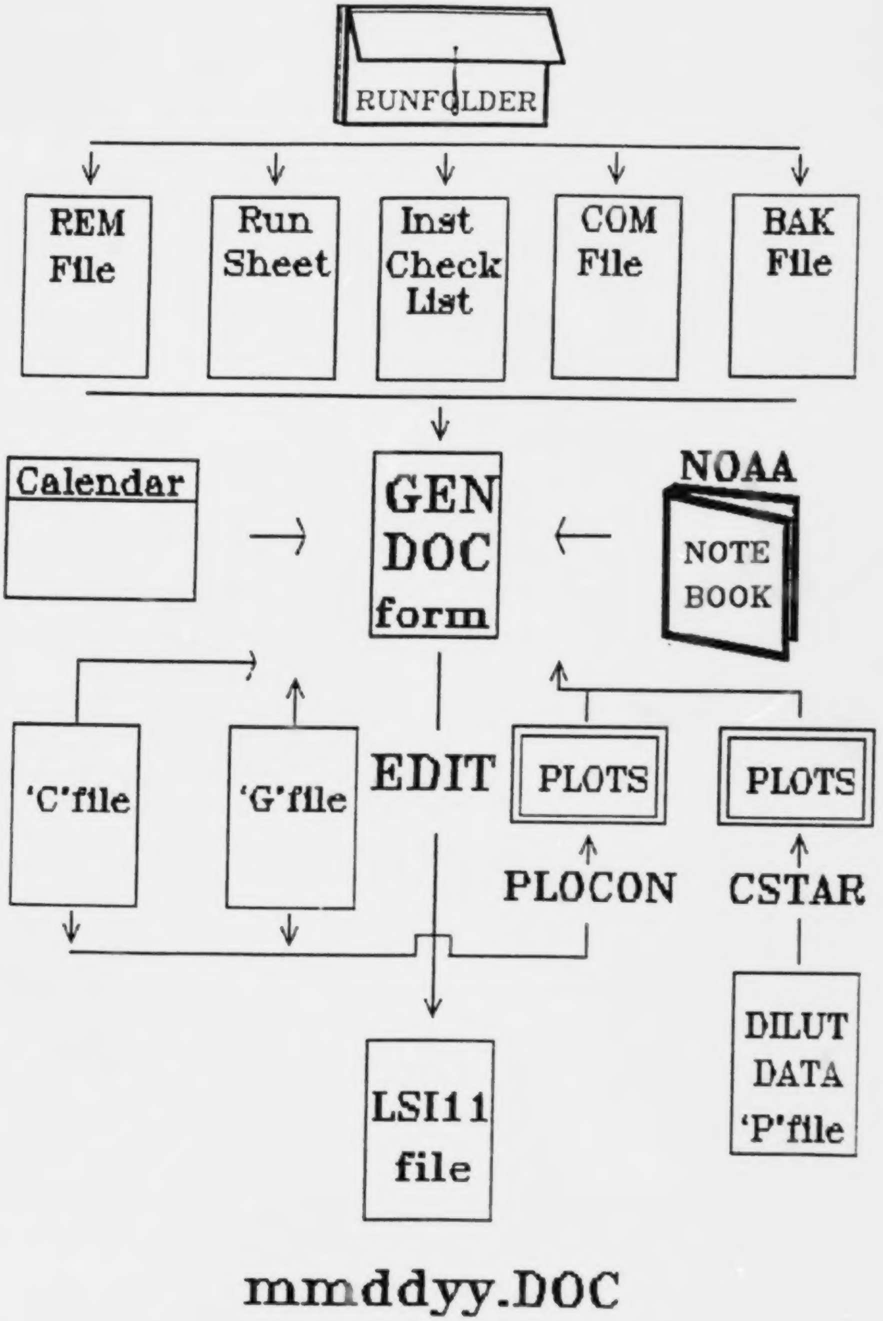

RUNFOLDER
REM File
Run Sheet
Inst Check List
COM File
BAK File
Calendar
GEN DOC form
NOAA
NOTE BOOK
'C'file
'G'file
EDIT
PLOTS
PLOTS
PLOCON
CSTAR
DILUT DATA 'P'file
LSI11 file
mmddyy.DOC

**Figure 25.** Documentation Processing Flowchart (Computers and Files)

## Initial Conditions

The initial conditions of the experiment are listed next. Concentrations for each species for each side are listed. These values are obtained from the "G" and "C" files, usually at sunrise. If the initial conditions are from data taken after sunrise then the data time is reported. Initial conditions are updated in `RUNENTRY` in the general section.

## Meteorological Conditions

Next the general meteorologial conditions (solar radiation and temperature) are indicated. Detailed data from NOAA reports and TSR stripcharts are the basis for a general ranking value computed for both before and afternoon.

### *TSR data compared against RDU data*

Total solar radiation data are compared with the NOAA data collected at the nearby RDU airport. The data profile for the experiment recorded at the site is inspected for "holes". A 1 to 10 grading scale is used to rate the experiments solar radiaion. The holes are counted and used to assess the grade value for both morning and afternoon portions (the morning sun is thought to be more important).

### *Temperature compared against RDU airport data*

The temperature at sunrise and at the maximum is compared with the RDU airport data for consistency and listed.

## Data Times, Data Exceptions, Special Problems and Concerns

The times that the initial conditions are established, sunrise time and when the experiment ends are given. Data exception are listed. Special problems and concerns are listed.

## Quality Assessment

An overall quality assessment grading scale has been devised to help compare the large number of experiments. The index ranges from 0 to 10 with 10 being a perfect experiment. Although the assessment of the quality index is somewhat subjective, many characteristics can be quantified relatively. There are five categories which are each weighted equally.

### *Solar Radiation*

For the earlier years of the dataset sun light was the principle factor used for representing run quality. Starting in 1981 more formal methods were developed: a formula which would grade the sunlight quality more consistently but with the same general techniques used earlier: a) the percent of possible solar radiation measured for the day, b) the number "holes or dips" in the radiation profile, and c) morning fog or haze. The earlier sunlight profile of the day is usually considered more import than the post solar noon portion. Therefore the first half of the day is weighted 70of the total quality index. Meteorological data obtained at a local major airport (RDU) lists percent of possible sun data which has been found to correlate well with observed solar profiles and is used to establish the base index value: 90 percent is converted to a quality index of "9". Then "holes" (25 percent or more attenuation of expected intensity) are divided and counted into three classes: 15, 30 and 60 minute duration. Index units are subtracted for each "hole" weighed by duration class.

### *Target Conditions Established*

There are three general areas of concern: a) whether target conditions were obtained, b) whether the internal (one side consideration) and external ratios (two sides compared) for each key condition parameter were obtained, and c) whether the experimental conditions are quantifiable or verifiable.

The base sub-index is set at "10". One index unit is deducted for each 20 percent error from the absolute target condition desired. Very often with the dual smog chambers it is the relative ratios of the initial component concentrations that is more important. There are two types of relative comparisons which are made: the ratios of components to each other within a mixture and the ratios of components in two different mixtures (side by side comparison). If a mixture is used, the relative fractions of components often needs to be carefully established. Very often the initial condition of interest is a matched HC to NOx ratio. One index point is deleted for each 5 percent error from the target relative composition.

Usually initial conditions are verifiable analytically. When an analytical techniques fails or a sample is not taken before the beginning of an experiment, other techniques may have to be used to establish or estimate the initial conditions. Direct injection of neat liquids or gases are often used as a calibration technique and therefore can be used as a second best estimate of initial conditions. If a component of a commonly used mixture is not directly analytically monitored for a particular experiment, its concentration can be estimated from the concentrations of the other mixture components and relative composition data. However these techniques are less than ideal and two index units are deleted from this quality category for each compound not verified by an analytical technique.

### *Analytical Support*

Analytical support is not always available for all species for all runs: techniques sometimes fail during an experiment. The base index is set at "10" and index points are deleted weighed by importance of the species or physical data not measured.

### *Chamber Conditions*

Chamber conditions can have a major impact on experimental results. Important parameters include: a) condensation on walls, b) dilution rate, and c) hours of venting before the experiment. The base index is set at "10".

Condensation observed on chamber walls is noted by the operator starting the experiment. One index point is deleted if condensation is observed on both chambers. Chamber driers do not always operate well and sometimes one side may be dried better than the other resulting in condensation in one side only. Two index units are deleted for this situation.

Dilution rate is usually monitored by use of inert tracers such as CCl4. A exponential least-squares fit analysis yields the dilution rate (necessary for proper modeling) for each chamber. The quality index is deleted by one if the dilution rates differ by more than 20 percent. Additional points are deleted proportionally for dilution rates exceeding the normal dilution rate of 1.5 * 10-4 min-1. The index is deleted by two if the dilution rate is not quantifiable (incomplete of poor tracer data). The quality index is deleted by one if the dilution rate is high or irregular from windy conditions. Dilution rates are normally well matched and less than 10 percent per ten hours.

Two hours of venting will eliminate observable concentrations of chamber pollutants. Regular experimental protocol requires that each run by preceded with at least six hours of venting. Three index points are deleted if less venting time is used.

### *Overall Value—Need*

Other major aspects of an experiment are overall usefulness and value. Many experiments are conducted to satisfy questions requiring immediate attention or special effort. Often these experiments are difficult to conduct; the experimental quality may be less than desired but nevertheless contributes usefull information which may be otherwise impossible to obtain. These experiments may be supportive of other experiments. This category is used to adjust the quality index to reflect these experimental needs.

### Documentation File Production

When all of the documentation information has been collected and the GENERAL DOCUMENTATION form has been filled out, the PC updates RUNENTRY with the SUM event. This will indicate to the CT that documentation information is ready to be moved to the VAX11/780. The CT uses a template file and a text editor. When the documentation file is produced, the CT updates RUNENTRY with the D2V event. This indicates to the PC in the next PCREPORT that the documentation file is ready for final QA. The file is listed and stored in the RUNFOLDER.

The listed documentation file is compared with the GENERAL DOCUMENTATION form to be sure that at least the information was correctly transfered. The documentation information is checked one last time with general experimental results: plots of the experimental data are compared with the initial conditions for consistency of relative reactivity. The stated initial conditions and the data plots should be checked for agreement. The quality indices for sunlight should be compared with the light plots for reasonableness. The general run quality index should be checked for overall reasonableness having read the documentation and looked at the data plots. If it is low, the reasons should be apparent in the documentation (*e.g.*missing data, chamber condensation present, or poor sunlight).

When the QA criteria are satisfied, the PC updates RUNENTRY with the DQA event. The GENERAL section of RUNENTRY is updated with the final initial conditions and the quality index value. This is usually the last step before producing the final segmented file.

## Final Segmented File Production

When all data processing tasks are completed, the files are moved to the VAX11/780. The files are merged together with a procedure called FINALMRG which follows a prescribed order. An ASCII labeled tape is made. Plots are made from the segmented file as a QA step: if the format is incorrect the plotting programs will probably not be able to read the file. The file is listed and inspected. The RUNENTRY event flowchart is shown in Table 21.

## Table 21.

### Final Segmented File Production Steps

```
FINAL FILE data processing steps
Pers     Step                      Meaning
----     ---------------------     -----------------------------------
CT       MR3 : Merged 3 sect       Merge pieces to final file
CT       ALT : Files to tape       Ascii labeled tape made
CT       FPC : Final plot done     Correct conc plot made
PC       FQA : Final QA            Final Quality Assurance
PC       NTB : Not to be proc
PC       BAD : Stop processing     Something is wrong with this data
```

## Security of Data

There are three basic activities to enhance data security: inventory, retention of original data to restricted areas, and maintaining several backup copies of all data in different locations. All data are under lock at night.

### Inventory

Before anyone is allowed to work with the run folder contents, a run folder inventory is performed which documents all data and forms. This helps assure that no data or documentation is lost.

### Retention of Data

All original data, both paper and electronic files are retained. Paper formated data (all stripcharts, forms) are not allowed out of the office.

### Backup of Data

Multiple copies of data are maintained in several formats in several locations. Backup copies of raw and final data on floppies on the `IBM PC` are kept in several locations. Lotus worksheet files are backed up in two locations. Hardcopy (printouts) of worksheet formulas using a spreadsheet `AUDITOR` is kept. Backup copies of raw and final data on `LSI11/23` computers are maintained in several locations, including: raw data and processed data sets backed up on two diskettes, processing programs (sources) backed up on two diskettes, and whole image harddisk backup of `LSI11/23`. Backup copies of final data are maintained on the `VAX` and further backed-up on tapes of `VAX` files. Frequent printouts of of data in all stages of processing ("P"-, "C"-, and "K"-files) and plots are kept in runfolders and in notebooks.

# 5

# Segmented Data File

This section describes the final segmented data file used for distribution of the experimental results.

## General Description

All of the data for a run are stored in a single file. This includes: documentation including the calibration information; the continuous instrument data, every 4-minutes, alternating on chamber sides in physical units; and the gas chromatographic instrument data given in concentration units for each side of the chamber for each instrument approximately every 30 minutes.

## File Formats

No record exceeds 80 columns (data is in "card image") form. The general lay out of the file is:

```
DOCUMENTATION  segment <starts with first record>
      GENERAL DOCUMENTATION
88888 <documentation section terminator>
      first instrument documentation ''K-file'' section
88888 <documentation section terminator>
      second instrument documentation ''K-file'' section
88888 <documentation section terminator>
  ...           .....
88888
      last instrument documentation section
88888 <terminator>
      DVM data documentation section
99999    <END OF DOCUMENTATION SEGMENT>
      DVM Data, up to 3 'cards' per time
99999    <END OF INSTRUMENT DATA SEGMENT>
      First instrument data, up to 3 'cards' per time
99999    <END OF INSTRUMENT DATA SEGMENT>
      Second instrument data
99999    <END OF INSTRUMENT DATA SEGMENT>
  ...           .....
99999     <END OF FILE>
```

An example segmented data file is shown in Table 22.

## ANSI Tape File Format

The segmented data files are written one file after the other onto 1/2 inch wide industry standard magnetic tape at a density of 1600 bits per inch.

We have adopted the American National Institute of Standards (ANSI) standard labeled tape format. This format is supported by a wide variety of computers including most mini-computers, and IBM. An advantage of a labeled tape is the "directories" of the tape contents can easily be created without having to list the data.

Individual records of the files are collected together into a "block" of records before being written to the tape. They can appear on the tape in one or two forms:

## Table 22. Example Segmented Data File

```
                          GENERAL DOCUMENTATION

RUNDATE: OCTOBER 04, 1983

RUNTYPE: AUTO

RUN DESCRIPTION: COMPARISON OF REACTIVITY OF EXHAUST
FROM DIRECT INJECTION FROM DODGE CHARGER IN HIGH IDLE
WITH SYNTHETIC AUTOEXHAUST.

RESULTS: TWO SYSTEMS RESULTED IN SIMILAR REACTIVITY

INITIAL CONDITIONS:              BLUE         RED
DODGE CHARGER                    0.0          2.587
SYNTHETIC EXHAUST NMHC           2.190        0.0
NO                               0.214        0.215
NO2                              0.037        0.039
.
.
.
88888
04-OCT-83                                      GENERATED ON 19-MAR-84
SY:OC043K.C1G       .C1G
PICKED DATA ENTERED BY JEFFREY HOFFNER
CALIBRATION FACTORS APPLIED BY CHARLES
TOLUENE                             2.912000E-01    PPMC/IN      2     KGS
ETHYLENE                            9.020000E-02    PPMC.IN      2     KGS
.
.
NAME ABBREVIATIONS - SAME ORDER AS IN DATA
TOLUENE    IS TOLUENE                          MAX A:   1.5610 MAX CON:   0.4546
ETHYLENE   IS ETHYLENE                         MAX A:   4.9164 MAX CON:   0.4435
.
.
```

### Table 22, cont. Example Segmented Data File

```
88888
04-OCT-83                                          GENERATED ON 13-MAR-84
SY:OC043K.C2G        .C2G
PICKED DATA ENTERED BY JEFFREY HOFFNER
CALIBRATION FACTORS APPLIED BY JEFFREY HOFFNER
ETHANE                                   1.498000E-01    PPMC/IN      2     KGS
PROPYLENE                                7.307000E-01    PPMC/IN      2     KGS
.
.
NAME ABBREVIATIONS - SAME ORDER AS IN DATA
ETHANE    IS ETHANE                              MAX A:    0.2014 MAX CON:    0.0302
PROPYLENE IS PROPYLENE                           MAX A:    0.1311 MAX CON:    0.0958
.
.
88888
.
.
.
88888
USER DOCUMENTATION FOR RUN 831004
.
.
CALIBRATION FACTORS USED:
SPECIE
 TIME      INTERVAL   BEGINNING    GAIN      ENDING   BEGINNING    OFFS      ENDING
                        GAIN       SLOPE      GAIN     OFFSET      SLOPE     OFFSET
  HR          HR                   HR-1                            HR-1
03G
  2.500     15.500     1.01380    0.00000    1.01380    0.00000    0.00000    0.00000
 18.000      6.000     0.00000    0.00000    0.00000   -9.99999    0.00000   -9.99999
.
.
END OF PROGRAM DOCUMENTATION
99999
YYMMDDHHMM     U     S    O3G        NOG        NOXG       NO2G       DPG        CTMP
     LTMP      TSR        UV
8310040500     1    7R    0.0008     0.0864     0.1138     0.0237     50.0450    56.8300
   58.6810   -0.0046     -0.2439
8310040504     1    3B    0.0196    -0.0022    -0.0007     0.0001     56.6496   -60.5560
   21.6880   -0.0062     -0.2439
.
.
```

## Table 22, cont. Example Segmented Data File

```
.

.

8310041704     1   3B     0.5787    -0.0012     0.0513     0.0507    72.7266   -60.5120
   20.5120     0.1592   11.7073
8310041708     1   7R     0.5508    -0.0013     0.0578     0.0573    64.7658    83.3620
   81.3040     0.1376   10.2439
99999
YYMMDDHHMM    USER SIDE      GENERATED ON 19-MAR-84
2,4,4 TRI TOLUENE   ETHYLENE  N-BUTANE  TRANS-2-B ISOPENTAN N-PENTANE ACETYLENE
8310040625     1    B
   0.2266     0.4546     0.4435     0.0877     0.0366     0.1339     0.0000     0.0905
8310040655     1    R
   0.1868     0.2580     0.2248 -999.0000     0.0459     0.1195     0.0634     0.2332
.

.
8310041455     1    R
   0.1439     0.1573     0.0890 -999.0000     0.0000     0.0828     0.0340     0.1672
8310041525     1    B
   0.1821     0.2514     0.1300     0.0688     0.0000     0.0921     0.0000     0.0000
99999
YYMMDDHHMM    USER SIDE      GENERATED ON 13-MAR-84
ETHYLENE  ETHANE    PROPYLENE
8310040625     1    B
   0.4522     0.0093     0.0952
8310040655     1    R
   0.4097     0.0238     0.0958
.

.

8310041525     1    B
   0.1603     0.0086     0.0000
8310041555     1    R
   0.2675     0.0260     0.0000
99999
```

fixed length, blocked rocords, or variable length, blocked records. The default value is fixed length blocked records with a record size of 80 bytes and a block size of 2000 bytes. For variable length records, the records are between 5 bytes and 84 bytes, and the block size is 2048 bytes.

Figure 26 to 33 and Tables 23 to 26 explain the details of the ANSI tape format as an aid in reading the tape. Volumn identifiers on the ANSI tape (in the VOL1 label field are UNC001 to UNC010 depending upon the release.

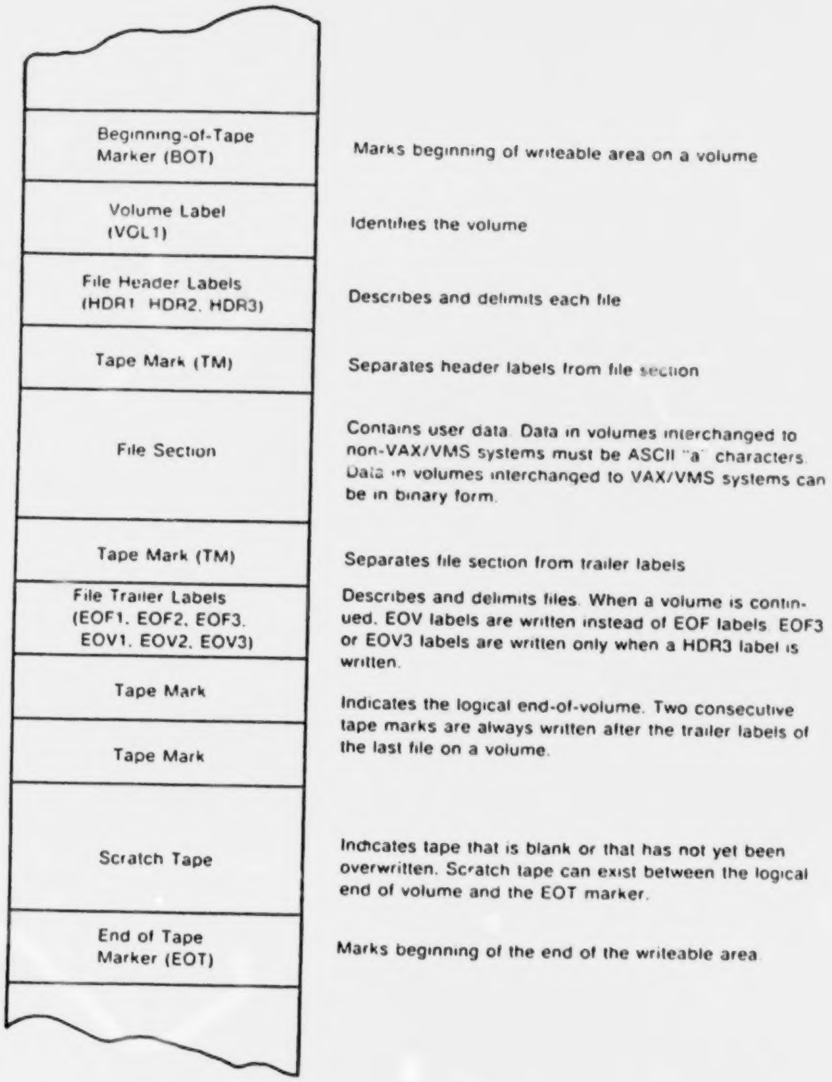
File identifiers on the ANSI tape (in the HDR1 label format) are YYMMDD.SEG for the year, month, day of the run.

## Tape Contents

## Final Data Plots made from SegFile

Although all processing of data and documentation is subjected to many QA procedures, the final SegFile is inspected and tested. The file is listed and inspected for order and completeness of the SegFile components. This is also a last chance look at the general documentation and format of the data files.

The final product is intended to be read by computer. The final QA test is using a computer program to read the SegFile and produce plots of the data to demonstrate that the file is correct and to examine the data visually.



| | |
|---|---|
| Beginning-of-Tape Marker (BOT) | Marks beginning of writeable area on a volume |
| Volume Label (VOL1) | Identifies the volume |
| File Header Labels (HDR1 HDR2, HDR3) | Describes and delimits each file |
| Tape Mark (TM) | Separates header labels from file section |
| File Section | Contains user data. Data in volumes interchanged to non-VAX/VMS systems must be ASCII "a" characters. Data in volumes interchanged to VAX/VMS systems can be in binary form. |
| Tape Mark (TM) | Separates file section from trailer labels |
| File Trailer Labels (EOF1, EOF2, EOF3, EOV1, EOV2, EOV3) | Describes and delimits files. When a volume is continued, EOV labels are written instead of EOF labels. EOF3 or EOV3 labels are written only when a HDR3 label is written. |
| Tape Mark | Indicates the logical end-of-volume. Two consecutive tape marks are always written after the trailer labels of the last file on a volume. |
| Tape Mark | |
| Scratch Tape | Indicates tape that is blank or that has not yet been overwritten. Scratch tape can exist between the logical end of volume and the EOT marker. |
| End of Tape Marker (EOT) | Marks beginning of the end of the writeable area. |

**Figure 26.** Basic Layout of a VAX/VMS ANSI Labeled Volume

Labels and Components Supported by VAX/VMS

| Symbol | Meaning | Symbol | Meaning |
|---|---|---|---|
| BOT | Beginning-of-tape marker | EOV3 | Third end-of-volume label |
| EOF1 | First end-of-file label | HDR1 | First header label |
| EOF2 | Second end-of-file label | HDR2 | Second header label |
| EOF3 | Third end-of-file label | HDR3 | Third header label |
| EOT | End-of-tape marker | VOL1 | Volume label |
| EOV1 | First end-of-volume label | TM | Tape mark |
| EOV2 | Second end-of-volume label | TM TM | Double tape mark indicates an empty file section or the logical end-of-volume |

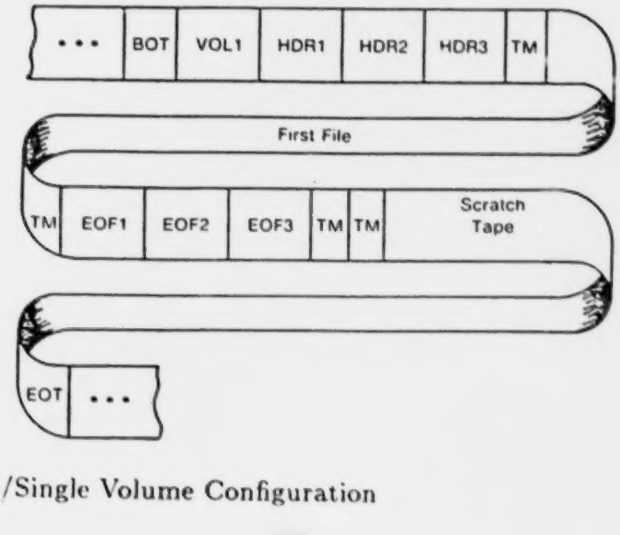

...
BOT
VOL1
HDR1
HDR2
HDR3
TM
First File
TM
EOF1
EOF2
EOF3
TM
TM
Scratch Tape
EOT
...

**Figure 27.** Single File/Single Volume Configuration

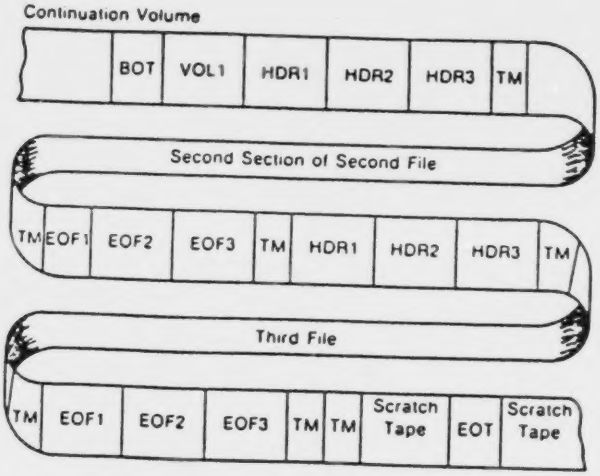
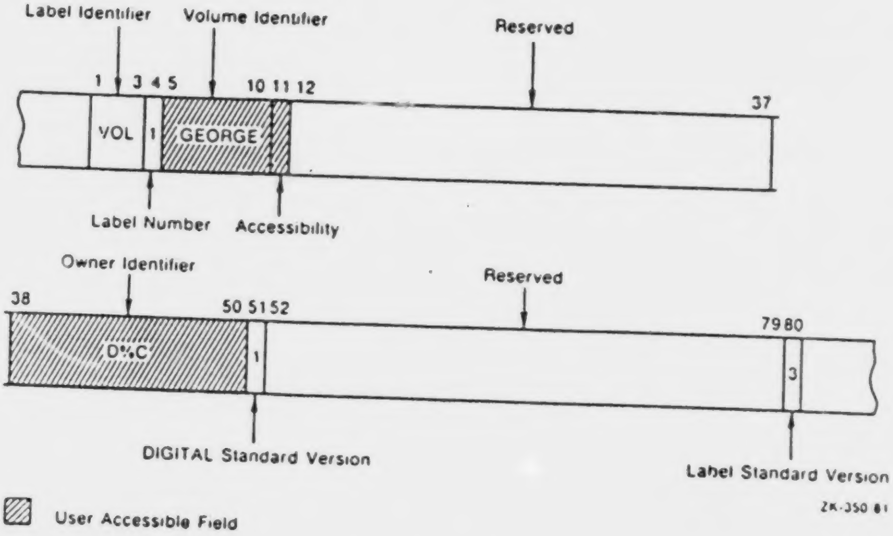

Continuation Volume
BOT
VOL1
HDR1
HDR2
HDR3
TM
Second Section of Second File
TM
EOF1
EOF2
EOF3
TM
HDR1
HDR2
HDR3
TM
Third File
TM
EOF1
EOF2
EOF3
TM
TM
Scratch Tape
EOT
Scratch Tape

Figure 28. Multifile/Multivolume Configuration


Label Identifier
Volume Identifier
Reserved
1
3
4
5
10
11
12
37
VOL
1
GEORGE
Label Number
Accessibility
Owner Identifier
Reserved
38
50
51
52
79
80
D%C
1
3
DIGITAL Standard Version
Label Standard Version
User Accessible Field
ZK-350-81

VAX/VMS ANSI VOL1 Label Format

Figure 29.

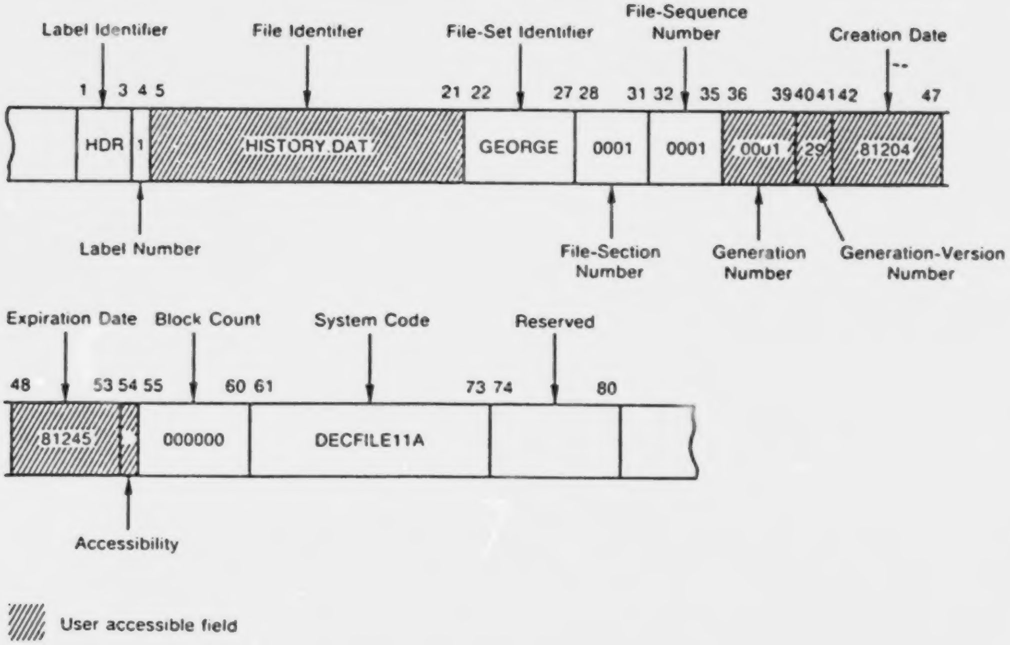

Label Identifier
File Identifier
File-Set Identifier
File-Sequence Number
Creation Date
1 3 4 5
21 22
27 28
31 32
35 36
39 40 41 42
47
HDR
1
HISTORY.DAT
GEORGE
0001
0001
0001
29
81204
Label Number
File-Section Number
Generation Number
Generation-Version Number
Expiration Date
Block Count
System Code
Reserved
48
53 54 55
60 61
73 74
80
81245
000000
DECFILE11A
Accessibility
User accessible field

**Figure 30.** HDR1 Label Format

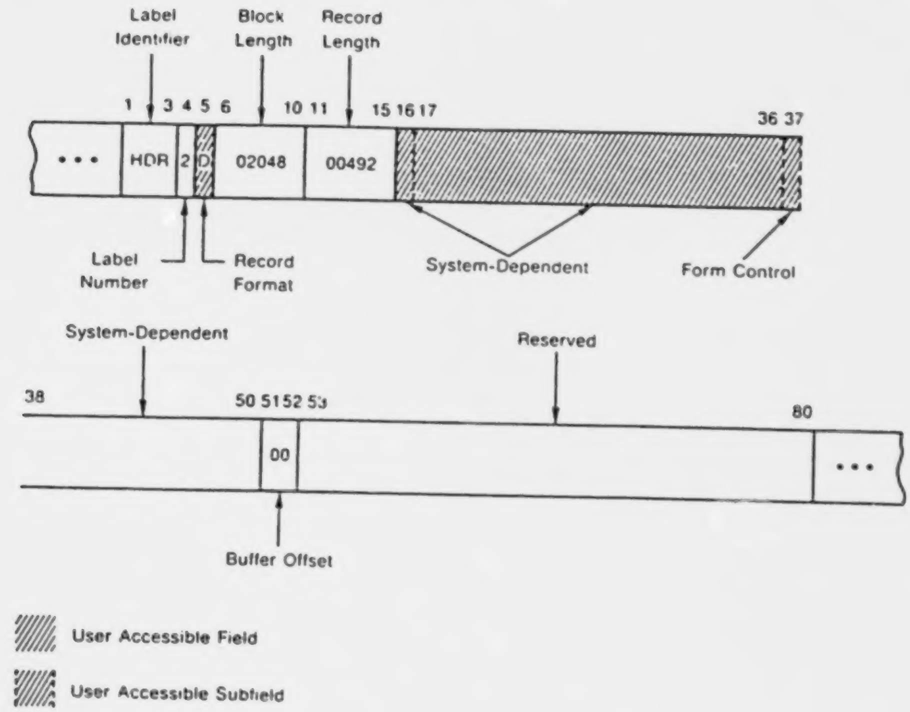
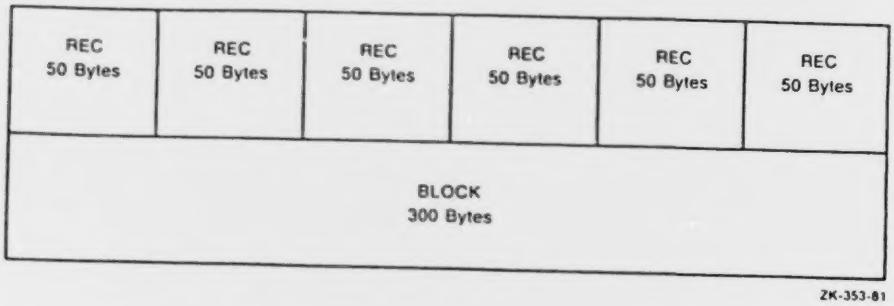
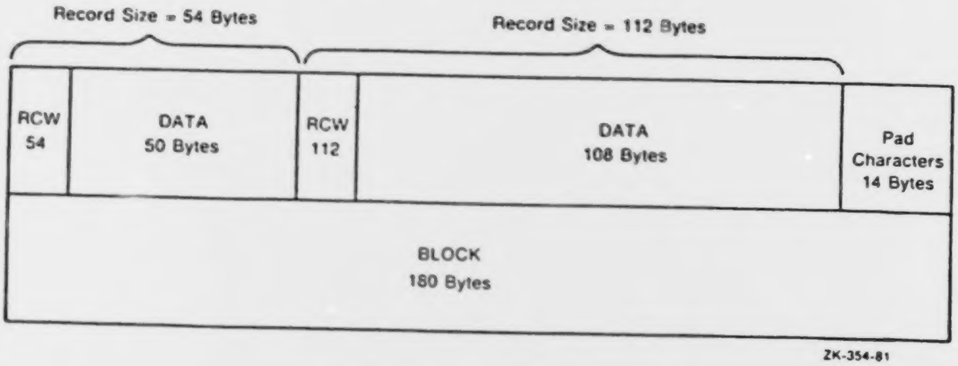

Label Identifier
Block Length
Record Length
1
3
4
5
6
10
11
15
16
17
36
37
• • •
HDR
2
D
02048
00492
Label Number
Record Format
System-Dependent
Form Control
System-Dependent
Reserved
38
50
51
52
53
80
00
• • •
Buffer Offset
User Accessible Field
User Accessible Subfield

**Figure 31.** HDR2 Label Format


REC
50 Bytes
REC
50 Bytes
REC
50 Bytes
REC
50 Bytes
REC
50 Bytes
REC
50 Bytes
BLOCK
300 Bytes
ZK-353-81

Blocked Fixed-Length Records


Record Size = 54 Bytes
Record Size = 112 Bytes
RCW
54
DATA
50 Bytes
RCW
112
DATA
108 Bytes
Pad
Characters
14 Bytes
BLOCK
180 Bytes
ZK-354-81

Variable-Length Records

**Figure 32.** Blocked Fixed-Length Records

**Table 23.** VAX/VMS ANSI VOL1 Label

| Character Position | Field (length in bytes) | Contents |
|---|---|---|
| 1 - 3 | Label Identifier (3) | Alphabetic characters VOL |
| 4 | Label Number (1) | Numeric character 1 |
| 5 - 10 | Volume Identifier (6) | Volume label consists of ASCII "a" characters. |
| 11 | Accessibility (1) | Volume accessibility; provides compatibility with some non-VAX/VMS systems. A space, the VAX/VMS default, indicates no restrictions. To write any ASCII "a" character in this field, use /LABEL=VOLUME_ACCESSIBILITY with the INITIALIZE command. Any character but a space indicates the /OVERRIDE qualifier must be used with the INITIALIZE and MOUNT commands. |
| 12 - 37 | Reserved (26) | Spaces |
| 38 - 50 | Owner Identifier (13) | Volume ownership set by the INITIALIZE/PROTECTION command. The contents of this field are used for volume protection |
| 51 | DIGITAL Standard Version 1 | Numeric character 1 |
| 52 - 79 | Reserved (28) | Spaces |
| 80 | Label Standard Version 1 | Numeric character 3 |

**Table 24.** First File Header Label (HDR1) Fields

| Character Position | Field (length in bytes) | Contents |
|---|---|---|
| 1 - 3 | Label Identifier (3) | Alphabetic characters HDR |
| 4 | Label Number (1) | Numeric character 1 |
| 5 - 21 | File Identifier (17) | A user-supplied file name and file type |
| 22 - 27 | File-Set Identifier (6) | Same as the file-set identifier of the first file on the first volume, whether single or multivolume configuration |
| 28 - 31 | File-Section Number (4) | Numeric characters starting at 0001 and incrementing by 1 for each additional volume with respect to the first volume on which the file begins |
| 32 - 35 | File-Sequence Number (4) | File number within the volume set for this file; consists of numeric characters, starting at 0001 that indicate the position of this file with respect to the first file of the set |
| 36 - 39 | Generation Number (4) | Numeric characters that indicate the unique generation of a file |
| 40 - 41 | Generation-Version (2) Number | Numeric characters that indicate the version of a particular generation of a file |
| 42 - 47 | Creation Date (6) | System stores the date in the Julian format (#YYDDD)[1]; the default is the current date |
| 48 - 53 | Expiration Date (6) | User specified Julian date (#YYDDD)* or default is the creation date, indicating file expires immediately |
| 54 | Accessibility (1) | File accessibility; provides compatibility with some non-DIGITAL systems. A space (used by DIGITAL systems) indicates no restrictions. Any character but a space indicates the /OVERRIDE qualifier must be used at mount time for the user to access this file. |
| 55 - 60 | Block Count (6) | Always 000000 for the HDR1 label |

1. The number sign (#) in the Julian format represents a space.

(continued on next page)

Table 24. (Cont.): First File Header Label (HDR1) Fields

| Character Position | Field (length in bytes) | Contents |
|---|---|---|
| 61 - 73 | System Code (13) | Identifies the file system that created the file. DEC, the 3-character constant, occupies positions 61 through 63, followed by the name of the file system; DECFILE112 indicates VAX/VMS Version 1.6 and earlier, and DECFILE11A indicates VAX/VMS Version 2.0 and later. |
| 74 - 80 | Reserved (7) | Spaces |

Table 25. Second File Header Label (HDR2) Fields

| Character Position | Field (length in bytes) | Contents |
|---|---|---|
| 1 - 3 | Label Identifier (3) | Alphabetic characters HDR |
| 4 | Label Number (1) | Numeric character 2 |
| 5 | Record Format (1) | Character definition:<br>F fixed-length<br>D variable-length<br>The S for spanned record format is returned as an undefined format when processed by VAX/VMS[1] |
| 6 - 10 | Block Length (5) | Five numeric characters specifying the maximum number of characters per block |
| 11 - 15 | Record Length (5) | Numeric characters indicating the record length for fixed-length records or the maximum record length for variable-length records |
| 16 | System-Dependent (1) | In VAX/VMS Version 2.1 and later versions, this field contains a space indicating the VAX-11 RMS attributes are in the HDR3 label<br>For VAX/VMS Version 2.0 and previous versions, this field does not contain a space but contains the first byte of the VAX-11 RMS attributes, indicating the VAX-11 RMS attributes are in the HDR2 label |

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[1] To process undefined records properly, the user must know what the original format of the records was. Only logical I/O can be used to process undefined record formats.

(continued on next page)

**Table 25.** (Cont.): Second File Header Label (HDR2) Fields

| Character Position | Field (length in bytes) | Contents |
|---|---|---|
| 17 - 36 | System-Dependent (20) | Spaces available for future use. For VAX/VMS Version 2.0 and earlier, this field contains the VAX-11 RMS attribute in binary format |
| 37 | Form Control (1) | Defines the carriage control applied to the records within a file, as follows:<br>A First byte of record contains FORTRAN control characters<br>M Record contains all form control information<br>Space Line feed/carriage return will be inserted between records (default) |
| 38 - 50 | System-Dependent (13) | Spaces available for future use. For VAX/VMS Version 2.0 and earlier, this field contains the VAX-11 RMS attributes in binary format |
| 51 - 52 | Buffer Offset (2) | The numeric characters 00 |
| 53 - 80 | Reserved (28) | Spaces |

**Table 26.** Third File Header Label (HDR3) Fields

| Character Position | Field (length in bytes) | Contents |
|---|---|---|
| 1 - 3 | Label Identifier (3) | Alphabetic characters HDR |
| 4 | Label Number (1) | Numeric character 3 |
| 5 - 68 | VAX-11 RMS Attributes (64) | Files-11 record attributes that override information in fields of the HDR2 label |
| 69 - 80 | System-Dependent (12) | Spaces |

# 6

# Summary of QA

## Summary of Calibration and Data QA

- 3 NBS traceable standards for NO were used in this project
- the three standards agreed at 3 concentration levels to within an average of 2.3 percent of each other
- 9 HC tanks and precision liquid chamber injections were used as calibration sources in this project; three of the HC tanks were NBS tanks from an RTI multi-year comparison study
- the four principle HC tanks, validated with the first two RTI tanks and liquid chamber injections, agreed to within an average of 1.6 percent of each other; and agreed to within an average of 3.7 (std dev 1.8 percent) percent to the manufacturers specified concentration values; the third RTI tank used in 1985 agreed within 1.8 percent of several of the other validated calibration sources
- HC calibration factors show very little or no trend in instrument sensitivity during the experimental season; the relative standard deviation from the mean calibration factors for the principle hydrocarbon species used in this project, ranged from 5 to 14 percent with an average of 9.9 percent (std dev 2.2 percent) in 1984 and ranged from 3.3 to 13.3 percent with an average of 6.6 percent (std dev 3.5 percent) in 1985.
- computer spreadsheets were used to adjust calibration factors (within observed "noise" range) to maintain consistency of experimental initial conditions composition produced from fixed composition (pressurized gas tank and liquid mixture) HC sources used in this project.
- two pressurized tanks of HC mixtures were used to produce the experimental initial conditions of the lower molecular weight compounds assuring consistent composition and initial concentration throughout the experiment series

- one of the principle HC source tanks for the experimental program (UNCMIX, a component of the synthetic urban mixture) is certified to 2 percent
- a liquid mixture of the higher molecular weight compounds was prepared and used throughout the program permitting one large neat injection to be made with 1 percent syringes to establish the experimental initial conditions: assuring consistent composition and initial concentration throughout the experiment series
- a multi-computer-based data acquisition and data processing system incorporated into a QA program which monitors every step of data generation and processing is utilized to minimize risk of human error and maximize accuracy and overall data quality.

## List of QA Steps

This section lists all specific QA steps performed.

### Before Runs

- review progress and schedule of experiments from work plan:
    - do experiments to date make sense? are they consistent?
    - do they indicate new experiments or other immediate needs?
    - are data for these experiments good enough or must they be rescheduled?
- check site status and weather report
- match highest priority experiment with immediate site capabilities
- fill out run sheets and instrument checklists
- use site checkout lists
- perform instrument checkout and calibration

### After Run–Experiment Logging

- PC phone call to site and update calendars:
    - verify general quality of run and conditions
    - reschedule?
- use "pack-up" inventory checklist at site

- check calendar for transfering data to floppies at site
- perform runfolder inventory
  - verify proper and complete documentation from site
  - verify complete data from site
- `RUNENTRY` - log experiment; store folder in office bookcase by date
- calibration folders - store in office bookcase by date
- `CALENTRY` - log any calibration performed
- calendar, run folder/`RUNENTRY`, fastplot in notebook check:
  - were runfolder and computer data transfered to data processing office?
  - successfully ?

## During Calibration

- planning:
  - what species will be measured; what calibration sources needed?
  - frequency?
  - technique?
  - documentation required?
  - procedure for transfering calibration data to dpo?
- identify standards and perform cross comparison:
  - check standards consistency
- `CALENTRY` - calibration log and processing status database:
  - during run log-in: check instrument checklist for calibrations performed or check for presence of calibration folder:
  - log calibration data in calentry
- routinely check `CALENTRY`:
  - check that all have been given processing instructions
- check documentation QA while giving processing (pick) instructions:
  - verify proper and complete documentation from site
- inspect calibration data stripchart for appropriate appearance
  - mark peak ids and chromatograms to pick
- routinely check `CALENTRY`:

  - check that all have been digpicked
- after DIGPIK inspect picked raw data on computer - compare with stripchart data
- routinely check CALENTRY:
  - check that all are run through CALFAC
- run CALLOK:
  - check report lists and plots to display results for representative compounds for early QA to identify any problems
- check DTR HCCAL database:
  - generate HCCAL report and scan entire report;
  - observe large variations and problems
- run CALANA: final check and statistical analysis
- during determination of calibration factors for data processing: does calibration result in meaningful data?

## During DVM Data Processing

- calendars and CTREPORT inspection:
  - are there data files missing?
  - new files to be unpacked?
- documentation comparison:
  - run sheet, instrument checklist, remarks file: what were target conditions?
  - any problems recorded?
- inspect stripchart:
  - were target conditions achieved (within calibration uncertainty)?
  - documentation complete? recorder settings, side, time for all pens?
  - does data make sense? are there unexplained problems? missing or noisy data?
- FASTDV plot and comparison with stripchart data
- AUTOCAL strip (see cal)
- AUTOCAL report:
  - did AUTOCAL data get processed?

  - any problems or large variation?
- run `DVMFIX`:
  - check that `DVMFIX` $NO_x$ concentration equals concentration of NO plus $NO_2$ all during experiment
  - check for good zeros
- QA `PLOCON` plots:
  - can plot file (format good)
  - data plot agrees with original stripchart
  - was data processed properly? correct times, sides, and general magnitude?
  - were holes processed properly?
  - dewpoint data higher than temperature?
  - does temperature data check with RDU airport?

## During GC Data Processing

- `PCREPORT` from `RUNENTRY`:
  - instruments needing pick instructions correct?
- documentation comparison:
  - inspect run sheet, instrument checklist, remarks file:
  - what were target conditions?
  - any problems recorded?
- inspect stripchart
  - instrument documentation complete? recorder settings, instrument atten, sides, time?
  - does data make sense? see run sheet:
  - is there missing or noisy data?
  - is data good? worth processing? bad?
  - identify calibrations and mark not to be processed as run data
  - identify compounds, pick start and end time, bad data to be skipped, baselines for peaks
- compare raw data stripchart and picked computer file:
  - is raw (picked) data picked correctly?

- `PLOPIC` plots (of raw data)
    - does data look reasonable? no side switching, attenuation switching problems?
    - sides id correct?
- after `CALCON`:
    - perform checks on C- and K-files and plots
- calibration factors and `RUNCALUSED`:
    - are calibration factors used consistent with others, or if not are they explainable?
- compare K-file with data processing instruction form
    - are the calibration factors used shown in K-file the same as specified in data processing instruction form?
    - are names of species correct?
- `PLOCON` plots:
    - can plot be made (file format correct)?
    - do plots seem reasonable?
- `HCANAL` or `LOTUS`:
    - if `HC` data for mixture, is composition consistent with known composition?
- run sheet target:
    - is resulting data consistent with target experimental conditions? or expected initial conditions?

## During Documentation Stages

- compare documentation:
    - inspect run sheet, instrument checklist, remarks file, calendars:
        - what were target conditions? any inconsistencies? may need to consult site operators (see run sheet)
        - any problems recorded?
        - special conditions, modifications, or operations performed?
        - missing data? species not measured?
        - how many hours of venting?

        - ▷ drying performed? condensation observed in morning?
- inspect stripcharts for notes of injection times or amounts
- check climate data, site temperature and light data:
- inspect data files and plots:
    - ○ how complete is data?
    - ○ explanations available for lost data?
    - ○ reason to communicate this to modelers?
- K-files check:
    - ○ documentation complete?
    - ○ any species co-eluting requiring documentation editing?
- compare original experiment list, general documentation paper form and run ranking formulas, and computer file:
    - ○ is information consistent or explainable?
    - ○ was experiment close to target? if not why not?
    - ○ is paper form with general documentation and formulas reduced and transfered correctly to computer file (general doc for segfile)?

### After SegFile Made

- verify file format and contents:
    - ○ by listing file and performing a visual inspection of the contents
    - ○ and by plotting data from file and inspecting plots

# References

1 Smog Chamber Background Reactivity, Part1: The Influence of $NO_x$ from Chamber Walls on Kinetic Computer Models for Air Pollution, submitted for publication

2 Smog Chamber Background Reactivity, Part2: The Influence of Radicals from Chamber Walls on Kinetic Computer Models for Air Pollution, submitted for publication

3 Code of Federal Regulations, Title 40, part 50, subchapter C, Appendix F, pages 568-572.

A

# Site Checklists

## Checklist For 0900 EDT Site Operator.

As you leave car walk by the red barn and pick up keys. A note pad for listing problems detected in checkout should be used.

### Outside Check

- Walk towards smog chamber on service-gas-tank-house-side of lab. Look at lab door. Are there any messages?
- Listen for Air generator pump running—pull back on metal plates protecting pump and inspect:
    - ○ are pumps upright?
    - ○ do they sound "right"?
- Quick check five service gas tanks (assuming BECKMAN THC is not operational): He, $H_2$ for Carles, $O_2$ for $NO_x$ meter, ethylene for $O_3$ meter, and $Ar/CH_4$ for Varian PAN instrument (generally need minimum of 100 lbs in tank to get through the day). While in the service tank house, check flood lamps mounted on wood chamber platform; if they are on, turn them off.
- Continue walking to BLUE chamber - walk to where manifold goes under chamber. Check service tank $N_2$ for AC driers air circulation valve actuators: secondary meter should show between 15 and 20 lbs and **NOT** higher or it will destroy pneumatic valves; note total lbs in tank and replace (later in the morning) if below 100 lbs.
- Touch heat tapes on BLUE Glass manifold: they should be warm. Inspect for condensation. Look along length of manifold including under chamber for large breaks or condensation. Visually check BLUE circulation fan over injection manifold in chamber: it should be running and turning smoothly.

- Walk to opposite side of chamber and observe venting doors (Make mental note of doors for comparison with run sheet which will be read shortly.
    - If there is no run then chamber is probably venting; all doors should be open and exhaust fan should be on.
    - If a "run" is on-going then in most cases all doors will be shut. Check RED exhaust door and make sure it is closed completely and door motor arm is positioned exactly like BLUE door motor arm.
    - If auto driers (AC system) is operational (one of the circulating fans will be on) then an intake door will be open.
    - If the dehumidifiers were used for drying they should have been removed before injections. If they have not, make note on the runsheet and call PC to determine if the experiment can be continued.
- Visually inspect for condensation both inside and outside the chamber on both sides (RED and BLUE). Rub hand over a large area of one of the side (not end) panels. Note any large drops of water or puddles on the floor of chamber. Note position of center teflon wall separating the chambers. Does it seem to hang more to one side than the other? Are all the fans running? Finally look for general problems such as mud (footprints), bugs, objects (tools, tape, paper towels, etc). in the chamber. Are the glass return and sample manifold intact? If the dehumidifiers were recently removed, were the service panels replaced and seated properly?
- Continue walking around the chamber to the other side back to the injection house and complete inspection of glass (RED) manifold. Feel heat tapes and inspect for condensation, breaks along length including under chamber. Is the RED thermistor laying on the ground?
- Go to BLUE side door in injection tank house. Observe if door is open or closed. It should be closed. Open door to inspect tanks, manifold, and solenoid plugs. Do not touch anything except the RED and BLUE injection lines! Do not turn off any tanks or touch any regulators. You will be coming out again shortly. Check that the RED and BLUE 1/4 inch Teflon injection lines are connected to the glass manifold. Check to see that they are tightly connected. Check to see if ALL computer controlled AC power boxes for solenoids have a plug in it (not including the light brown plastic box used for the WOOD project). They should also each have a light bulb.
- Close door and go to the other side; open door. Do any of the wires leading over the door catch? Quickly inspect this side of the injection shed for problems. Don't touch anything yet. Don't close any tanks yet. Is there a small wrench for turning off the $NO_2$ tank later? Close the door.

- Go inside the lab on the same side of building. Look up as you enter and notice if the outside floods are on. If they are turn them off with the switch just inside the door as you enter.
- Turn to the right as you enter and head for the $NO_x$ and $O_3$ strip chart. Look and observe if NO and $NO_2$ (or possibly $O_3$) have been injected. Notice approximate concentrations. Are conditions matched (generally)?
- Head for computer console (decwriter). Is the computer and DATCOL up? Are there error messages? Is there a print profile? If not, can you get the time of day from the computer? (Type TIME and return.)

  Are ALL switches in AUTO? Or is there a note saying some should be in MANUAL? Is the 4 minute clock in AUTO?
- Turn around and look for a filled out run sheet for today's run. What was the run today? Look at the command file printout if there is one. What was injected? What tanks were used? Did anything have to be injected or otherwise done manually? Was someone here this morning? See if morning operators name is filled in. Are there any notes on the desk?
- Does $NO_x$ and $O_3$ stripchart make sense compared to information on run sheet? Walk towards Carle GCs. Were injections made? Make quick inspection of chromatograms. Did anything show?
- Go outside to the injection shed (Carle side). Consider the run sheet, command file, $NO_x$ and $O_3$ stripcharts, and GC stripcharts. If injections were scheduled but failed, inspect tanks to see if they were turned on and connected to appropriate solenoids. Were they plugged in? R/B injection lines connected to the glass return manifold? If resulting injections seemed low, check flow rate. (Hastings mass flowmeter reads 8.7 for 10.0 lpm; check with soap bubble flowmeter with $N_2$).
- Once you are finished with the injection shed, turn off all tanks with the main valve. Do not turn off tanks with the regulator. Use a small wrench to close the $NO_2$ tank valve.
- Enter the lab again on the $NO_x$ and $O_3$ side. Go to the DVM and HP clock. Is the DVM scanning? If not, issue immediate command get time from the computer by typing TIME and return. Does the HP clock match? (If not set it later). Check 4 minute side light. Go over quickly to $NO_x$ and $O_3$ instruments.
- Check $NO_x$ and $O_3$ pressure (20) and vacuum pump pressure (25.5). Check $O_3$ ethylene (15) and rotoball setting. Mark stripchart with current side and time. Does it look like the 4 minute R/B switching valve is operating?

Perfect matched injections are almost impossible. If it looks like a perfect match, check the valve and the computer 4 minute switch again. Check that stripchart is marked properly for run date, instrument, stripchart settings, attenuation, *etc.*

- Is the HCHO instrument running? Should it be? Is the sample pump on? Is the rotoball at 4? Is the solutions pump on? Is it drawing solution? Are bubbles running through mixing/reacting chamber (below solutions pump). Check degasser chamber (on right side). It should not be filling up with liquid (a little bit at the bottom is ok). Check each sample line. Look at the HCHO stripchart. Does the signal trace look "right"? Check strip chart zero by pushing down black zero button: it should not be negative. If it is adjust it to about 10% of the chartscale. Adjust HCHO zero if necessary and make note on stripchart.
- Check waste container. Is it too full? Check that stripchart is marked properly for run date, instrument, stripchart settings, attenuation *etc.* Check dewpoint instrument stripchart. Check dewpoint stripchart zero. Mark it as zero check, and mark time and side. Is DP pump on? Is signal trace reasonable? IF there is a difference in dewpoint between the two sides the signal should be a square wave. If it shows a slow response, clean the detector and rebalance after letting it operate for a couple of minutes. If it looks O. K. , check balance. Walk to other side and move switch to test, wait for it to stabilize and adjust balance knob. Turn knob back to operate. Check that stripchart is marked properly for run date, instrument, stripchart settings, attenuation, *etc.*

### TSR and UV zero check

Mark time.

Check manifold on this side (RED). Start at the $NO_x$ and $O_3$ instrument end. (While you are at this end check zero air supply used for injections and be sure it is off.) Look for open fittings; missing caps or dangling sample lines. Feel heat tape; it should be warm. Look for condensation. Check zero air supply near stripchart for DP and HCHO. Move towards the other side of the bench. Check manifold fans to see that they are operating as you go around to the other side. Perform manifold check on this side walking to the end where the CARLEs are. Come back to the manifold fans. Check zero air supply. 100 lbs in and 60 lbs out. Check Tektronix terminal and clear screen by hitting page.

## GC Check

Check switch 6 on AUTO/MANUAL switch panel: is switch 6 on (Carles valve minders power)? Walk down towards Carles. On the way check the Varian stripchart. Are there injection peaks? H2O peaks? Tracer peaks? Is the sample pump on? Check that stripchart is marked properly for run date, instrument, stripchart settings, attenuation, *etc*. Check bucking current.

Are Carle valve minders in auto/repeat and sequencing? Do chromatograms look right? Air peaks? Look at example notebook if necessary. Are the GC sync? Do the chromatograms look right considering what was injected and the nature of today's run? Look at background chromatograms. Contamination? Ethylene? Was an autocal scheduled and were the chromatograms made? Peaks on scale for initial injection? Are they still on? Does it look like the baseline might drift off scale? Adjust with GC zero, not stripchart zero. Look at the service gas regulators. Do the readings match the numbers on the wall? Is the sample pump on? Is the 30 min RED/BLUE clock on and working? Is the flame lit? Reasonable attenuation getting? Are Sigma integrator reports being made?

Considering what was injected for the run:

- Target match condition? Are they matched?
- If difference, are the sides switching? Are both sets of chromatograms on scale (no peaks off scale)?
- If different amounts of same composition are ratios of peaks correct?
- Mark chromatograms with time and side. Try to mark time of sample injections.
- Try to mark when 30 min clock changes sides and whether B to R or R to B.
- Check that stripcharts are marked properly for run date, instrument, stripchart settings, attenuation, *etc*.

Check lab AC. Is it set at 72? Is fan in ON position (not AUTO)? When was the filter changed last? (It should be changed every three weeks.)

Enter PRINT PRO command if one is not printing already. Don't wait until later.

# Checklist for Leaving the Site Set Up for a Run

## Computer

Is the system up and ready?

- There has to be a day created on the disk for today in order for the system to run tomorrow.
- Create a day on the disk with tomorrow's date using the program "NEW-DAY". If necessary, create one for today also.
- Create a command file for tomorrow using the Program "CMANDR". Once you are satisfied, store the command file by hitting "W". Now run the command file thru "DATRAN" and merge ("RMERGE") it into tomorrow's DATCOL-OPS file.
- Run DATCOL, wait 1 minute and you should see a "*", which will tell you that DATCOL is up; hit <RETURN> and you should get another *. If there was a run today, key in "BACK". This will print out the commands for the current day and tell you if the restart commands to vent the chambers (Set 1,2,3,4) at 1900 are still in there; otherwise the chambers won't vent!!! If there was not a run today, issue an immediate command IMM <return> and Set 1,2,3,4; to open the chamber doors.
- Are all front panel switches in auto not manual position; DVM on auto, rear, remote.
- Is the 4 minute clock switched to auto and not locked on one side?
- Check decwriter paper. Need at least 10 pages.

## Formaldehyde

- Run on water for 15 minutes by placing all three reagent tubes in water.
- Loosen all four tubes on parastatic pump.
- Shut off two switches on rear of instrument starting from the right as you face the switches. leave left most switch on. This supplies charging "juice" to the instrument batteries.
- Make sure there is enough TCM stock reagent prepared (without sulfite) so that the person making the run in the morning just has to add 0.25 g sulfite to 200 ml TMC.

## NOx and O3 Instruments

- Are the 3-way valves for the O3 and NOx meters plugged into the 4-minute power strip?
- Is there a good connection between the NOx and O3 meter intakes and the round Teflon filters?
- Are the front panel settings of the O3 and NOx meters correct?
    - The NOx meter should be in ambient mode. NO, NO2, and NOx should be set to 1 ppm full scale. The oxygen pressure should be set at 20, and the valve knob should be set to NO-NO2-NOx. Vacuum gauge on NOx pump should read 26" Hg.
    - The O3 meter should be set to 2 ppm and full scale. The ethylene pressure should be on 15. The time constant on the instrument should be set to 10 sec. The top of the + ethylene flow rotoball should be set at 30, and the mode selector should be set on ambient.
    - Strip Chart Recorder:
        - ▹ Pens on; on "record"
        - ▹ Chart "on"
        - ▹ Voltages 1, 1, 1/2 for NO, NO2, O3
        - ▹ Chart speed 3 cm/hr and "on"
    - Autocal Tank:
        - ▹ Tank should be turned on, 5 psi showing on low side of regulator, and on/off needle valve on regulator turned on.
        - ▹ Flow should have been previously adjusted so that meter will have enough sample when span tank is turned on in the morning (rotoball is positive showing excess flow when meter is sampling from this apparatus.

## TSR and UV Chart

- Have the TSR and UV pens been properly zeroed?

## Charts

- Check that sufficient paper remains Red line will appear on paper when the roll is ending.

- Record the date, type of injection, attenuation, chart speed and scale of each instrument on the charts.
- Check that pens are full of ink and pens down.
- Check that power to charts works from AC switch no. 16 on blue computer AC switch panel. Activate no. 16 to manual and observe deflection on charts, return these to "auto" position.

## Carle I

- Is the G.C. up and running?
  - ○ Check pressure gauges on the wall behind the instrument H2 = 28.5 psi. He = 63 psi, air = 13.5 psi.
  - ○ Is the flame lit? (check by placing mirror or chromed surface over the FID. It should fog H2 pressure to 35 psi, hit ignite button; you should see positive response on strip chart (strip chart has to be on) after 5 minutes. Return H2 to 28.5 psi. Watch the gauge go down and make sure it stabilizes at 28.5 psi.
  - ○ Has the proper attenuation been dialed into Carle I? (X4 for mix, X8 for propylene and ethylene, everything else determined by the nature of the cal and the injection.
- Has the valve minder for Carle I been put on light no. 5 and a drum setting of 29?
  - ○ To check this, activate switch no. 6 on the computer.
  - ○ If the valveminder is not on light 5, switch the valveminder knob from "standby" to "sequence" at 10 second intervals until light no. 5 is on. While the valve minder know is in standby, rotate the timing drum until the face setting is 29. CHECK FLAME AGAIN. The valve minder knob should still be on standby at this time. Continue with Carle II and Carle III.

## Carle II and Carle III

- Is GC up and running?
  - ○ Check pressure gauges on wall. Carle II, He = 38 psi, H2 = 27.5 psi, Air = 12.5 psi. Carle III, He = 64 psi, H2 = 28 psi, Air = 13.5 psi.

    - Check to see if flame is lit (place mirror over the FID).
    - Check for proper attenuation (normally X4).
- Have the valve minders for Carle II and III been placed on light 8 and a drum setting of 59?
    - To check this activate switch 6 on the computer.
    - If light 8 is not on, switch valve minder knob from "repeat" to "manual" and activate "event advance", toggle switch until light 8 is on. WAIT 10 SEC. BETWEEN EACH ADVANCE SWITCH. Make sure that you see light no. 7 before you advance to light no. 8. Set the drum at 59. CHECK FLAME AGAIN. Return to the computer blue switch panel and switch no. 6 to "auto". NOW GO BACK TO THE CARLES AND SWITCH CARLE I FROM STANDBY TO AUTO.
- ALSO TURN THE VALVE MINDER ON CARLE II AND III TO REPEAT. DO NOT LEAVE IN SINGLE OR OFF!!!

## Sigma 10 Integrator

- If we want to collect integrator data on the Sigma 10, Carle I, II, III must be linked to the Sigma by a "set up" procedure.

```
      SIGMA          (your key strokes)
     Response         SET UP KEY ENTER
EXAMPLE:
(1,2,4)    1 Enter
method?
1(2,4)       Enter
mode         Enter
Sample ID  1 Enter
           Carle (no. ) enter
Ptr        1 Enter
```

Note that: Carle 1 - Inst 1, Method 1., Carle II = Inst 2, Method 2, Carle III = Inst 4, Method 4. PE 900 = Inst 3, Method 41.

- If PE 900 is to be used, is it set up? Instrument 3 Method 4.
- Is there enough paper in the printer?
    - There are 199 sheets total, so if the printer has less than 20 sheets left, change the paper.

  - Void plotter unless you want to use it, it will otherwise use a lot of paper.
- Clear out old SIGMA files by using the following keystroke sequence: Shift*F6 enter 200 enter or Shift *F Enter Enter. Hit the "Stat" key after this is done. You should have at least 1000 free blocks.
- Turn the Tekronics terminal off (this is the second channel to the Sigma).

### Dew Point Meter

- Has the dew point meter been balanced and returned to operate? Set to "Test" and balance indicator to center of scale.
- Has the detector been cleaned within a week? Using isopropyl alcohol and Q-tip on mirror in detector in rear of instrument.
- Is the dew point meter chart been properly zeroed?
- Is the 3-way valve for the dew point meter plugged into the 4-minute power strip?

### ATC and Varian

Check standing current in morning and afternoon.

- Set the ATC and Varian injection clock right before injection.
- Is the ATC and Varian injection clock plugged into charts?
- Check to see if the ATC and Varian sampling 3-way valve is plugged into the 30 min red/blue clock and if the Teflon lines from the 3-way valve are attached to the red and blue sampling manifolds.
- Is the correct attenuation dialed into the Varian (atten x*)?
- Is the correct attenuation dialed into the ATC (X26)?

### CO Meter

- Is the sample line on the gas chambers?
- Turn off service air tank Back on in morning.
- Are front panel switches in correct position?

## Air Generators

Must have 100 psi on input gauge, and 60 psi on output gauge.

## General

(CHECK INJECTION TANK FLOW WITH BUBBLE METER EACH DAY AND SET TO 10 L/MIN).

- Check tanks for tomorrow's injections.
    - Go to the injection house and remove the line for the tank to be used from its control outlet.
    - Plug this line into the white power cord and read the tank flow on the mass flow meter.
    - If the flow rate is low or high adjust it with the low side pressure regulator valve. All tanks should have a flow of 10 l/min including NO.
    - Plug the tank line back into the control outlet for that tank.
- Check the following tanks in the service gas house: O3 ethylene NOx oxygen, Carle I He and H2, Carle II He and H2, CO3 and H2; Varian: ArCH4.
- Liquid Injections
    - Determine the number of ul that have to be injected from the computer listed table on the wall in back of the formaldehyde instrument. This table tells you the number of ul that you have to inject into the chamber to give 1 ppmC. This has been computed for three different temperatures 60 F, 70 F, and 80 F. Selected the number ul to be injected from the list which will approximate tomorrow's morning temperature. Clearly write down the number of ul to be injected on the run sheet.
    - Locate the liquids to be injected and set them out in the work space of the hood. Find the liquid injection apparatus and clean the needed syringes so that the operation will not have to spend time doing this tomorrow. Place these on a clean paper towel by the injection ports of the return manifold.
    - If you have to calculate the no. of ul to get 1 ppmC of a liquid into the chamber use the following formula:
- Has the run sheet been filled out?

- Have the charts been marked with day, month, year, instrument, chart speed, full scale chart voltage, and attenuation and range where applicable?
- Check for loose or missing caps on the manifolds.
- Check the chamber recirculation fans.
- Check all the red blue 3 way valves connected to the GCs to make sure they are plugged into the 30-min power outlet.
- Final check
    - Check all auto/manual switches-computer and cal box-to make sure they are in auto position.
    - Check DVM to make sure it is in remote not local mode. Especially 4 minute clock; it should be in auto.
    - Check the red exhaust door on the chambers to see if it is the same as the blue exhaust door.
    - Make sure all charts are on and plugged into "charts" strip.
    - Check Carle I to be sure its valveminder is in auto and that Carle II and III valve minders are in repeat.
    - Check high Conc. NOx calibration tank to be sure it is off.
    - Check the Cal tank for the Carles to see that it is open.
    - Check injection tanks to seer that they are open and that the flow is correct.
    - Check the reagent levels for the HCHO instrument; also check the waste flask to see that it can't overfill.
    - Shut off water to toilet.
    - Make sure the chambers doors will open at 19:00, and vent by a Datcol Restart command, or by an immediate command to Datcol to set 1,2,3,4: before you leave the site.

## Early Morning Checkout

- Did the command file run? If not, see HELP LIST on end of rack over the DEC writer. Booting instructions are at other end of the rack over the disc.
- Is the DVM scanning? If not, issue an IMM to stop GASDVM; then, another IMM to start GASDVM. If DVM still is not scanning, switch from "Remote" to "Local", "Step" through to end of series (channel 60), return to "Remote" and issue an IMM to start GASDVM.
- Did the chambers vent? Check this by reading the $O_3$ strip chart–background should be almost completely free of $O_3$. If the chambers have not vented and enough time remains before sunrise–2.5 hours–manually vent chambers until just before sunrise. Close the chambers and then make all injections manually.
- Make CEA formaldehyde solutions.
- Read the run sheet and DEC printout of the day's command file to determine target concentrations.
- Find manual injection species and amounts and all apparatus necessary to make injections.
- Check chamber condensation and all vent doors (especially red exhaust door).
- Go to the injection house at the time of the injections to see if the lights confirm that the proper tanks are being injected. A list of tank concentrations, species, and switch numbers is on the end of the rack above the DEC writer.
- Check all charts.
    - ○ Charts on at charts.
    - ○ Pens down and full.
    - ○ Charts fully labeled.
    - ○ Sufficient chart paper for the day.
- Check manifolds to see that all caps are on and that each instrument is connected to both the red and blue manifolds.
- See that 4 minute computer clock is in AUTO and not locked manually to either side.
- Check status of SIGMA 10.
    - ○ "/STAT"; all Carles and PE 900 (if used) should be set up with the corresponding methods.
        - ▷ Carle 1 Method 1

        - ▷ Carle 2 Method 2
        - ▷ Carle 3 Method 4
        - ▷ PE 900 Method 31
    - ○ Check that sufficient paper remains for the day (about 75 sheets).
- Start CEA formaldehyde.
    - ○ On sample line
    - ○ Advanced past auto 0
    - ○ All pump lines connected and useable and pulling solutions.
    - ○ Sample pump on.
- Turn on air tank to the Beckman 6800 and turn on the instrument if it is to be used.
- Perform manual injections before 05:00 at the latest.
- Check standing current on the Varian: it should read about 600-9 x64 amps.
- Check injection concentrations and relate to target amounts by measuring peak heights and using the provided concentration conversion factors. See attached chromatograms.
    - ○ $NO_x$: additive value from strip chart or from DVM printout.
    - ○ Carle I,II,III: see attached chromatograms and respective values.
    - ○ Adjust concentrations of $NO_x$ or HC species, if necessary, to achieve desired amounts.
- Change attenuation on the Carles after the auto cal; generally, attenuation should be x2 or x4.
- Issue a PRINT PROFILE of the DVM data.
- After successful injection turn off injection tanks and successful auto HC span turn off HCspan tank.

## Run Pack-Up Checklist

Before a run folder is taken to school, check to see if the following items are in it:

1. Carle I and II stripchart
2. Carle III stripchart
3. Sigma 10 printout
4. Varian stripchart
5. Dewpoint stripchart
6. Beckman stripchart
7. PE900 stripchart
8. DNPH integrator Printout and stripchart
9. TSR and UV stripchart
10. Formaldehyde stripchart
11. $NO_x$ and $O_3$ stripchart
12. Run Sheet
13. Instrument Checklist
14. Profile Printout
15. Copy of command file used
16. Copy of BAKTRN of the day's OPS file

If one of these is missing note reason on the instrument checklist.

# B

# HC Cal Sources Certification

# APPENDIX B.

## COMPARISON OF HYDROCARBON CALIBRATION SOURCES

```
                                         Last Update:  13-Jun-85
RTI TANKS             PRIMARY STANDARD #1 AND #2

                               Species manuf.           Species manuf.
                                          conc.                    conc.
                            propylene 14.820          ethylene  20.000

                            27-Apr-78 14.580          27-Apr-78 19.400
                            22-May-78 14.820          25-May-78 19.200
                            23-May-78 14.340          10-Aug-78 19.800
                            08-Aug-78 14.940          05-May-80 16.800
                            14-May-80 14.790          19-Jul-81 20.000
                            03-Jan-84 14.400          29-May-84 19.000
ave USED                              14.645                    19.480

regression estimate         02-Aug-84 14.449          02-Aug-84 19.304
-----------------------------------------------------------------------
Calibration of Carles 1,2,3 with RTI tanks >> SIGMA 10 integrator ppmC/area

Assumption - these species are representative of average carbon response efficiency.
Did use May 5 1980 ethylene value.
Choice between regression value or average analysis value: used average.

                           UNC use:  14.645          UNC use:  19.480
Carle I              8/2/84 sigma 10  ppmc/area      sigma 10  ppmc/area
                                44.6  0.328              56.3  0.346
                                44.5  0.329              57.1  0.341
                                44.5  0.329              57.2  0.341
                                44.8  0.327
Ave
allave                                0.328                    0.343
                                                     0.335

                     8/1/84 sigma 10  ppmc/area
                                44.8  0.327

                                      0.327
```

```
Carle II          8/2/84 sigma 10  ppmc/area     sigma 10  ppmc/area
                            19.1   0.767            24.7   0.789
                              19   0.771            24.4   0.798
                            19.2   0.763            24.8   0.785
                            19.6   0.747            24.8   0.785
                            19.2   0.763            24.5   0.795
                            19.1   0.767
                            18.9   0.775

Ave                                0.765                   0.791
allave                                           0.778

                  8/1/84 sigma 10  ppmc/area     sigma 10  ppmc/area
                            17.4   0.842           25.31   0.770
                            19.2   0.763            24.7   0.789
                            19.3   0.759            24.7   0.789
                            20.5   0.714            25.2   0.773
                            19.3   0.759

ave                                0.767                   0.780
                                                 0.774

Carle III         8/2/84 sigma 10  ppmc/area
                            4.15   3.529
                            4.15   3.529
                            4.14   3.537
                            4.17   3.512
                            4.14   3.537

Ave                                3.529

                  8/1/84 sigma 10  ppmc/area
                            3.95   3.708
                            4.03   3.634
                            4.44   3.298

Ave                                3.547
```

```
-------------------------------------------------------------------------------------------------------
Airco Tank - Determination of Concentration based on RTI tank - analyzed same day
Date
                           toluene          ethylene          trans-2-butene      isopentane       propane          propylene
Carle I                      area     conc.   area                 area              area              area               area
8/2 - RTI ave ppmC/are 0.335

                            28.90                             21.30            28.00
                            29.90                             21.50            28.00            22.00           24.80
ave                         29.40    9.86                     21.40    7.18    28.00    9.39    22.00           24.90
                                                                                                22.00    7.38   24.65    8.34
8/1 - RTI ave ppmC/are 0.327

                            31.20
                            31.50                             22.70            29.70            23.60           26.20
ave                         31.35   10.25                     22.70            29.80            23.60           25.90
                                                              22.70    7.42    29.75    9.73    23.60    7.71   26.05    8.52

Carle II
8/2 - RTI ave ppmC/are 0.778

                                            4.75    3.69
                                                                                                 9.74    7.57   10.80    8.40
8/1 - RTI ave ppmC/are 0.774

                            16.20           5.08
                            14.50           4.83                                                10.60           11.60
                            14.20           4.75                                                10.30           11.40
                            14.70           4.81                                                 9.66           10.90
ave                         14.90   11.53   4.87    3.77                                         9.64           11.00
Carle III                                                                                       10.05    7.78   11.23    8.68
8/2 - RTI ave ppmC/are 3.529

                             3.22                              1.94             2.52
                             3.26                              1.96             2.55
ave                          3.24   11.43                      1.95    6.88     2.54    8.95
8/1 - RTI ave ppmC/are 3.547

                             3.30                              1.84             2.42
                             3.23                              1.90             2.47
                             3.24                              1.86             2.44
ave                          3.26   11.55                      1.87    6.62     2.44    8.67

THE AVERAGE -Airco tank             10.92           3.73               7.03             9.18             7.61            8.48
THE STD. DEV                         0.72           0.04               0.30             0.41             0.15            0.13
(these values are listed below - Airco Tank Final)
```

```
-----------------------------------------------------------------------------------------
CALIBRATION OF CARLES WITH AIRCO FOR ANALYSIS OF LOW AND HIGH MW HIGH CONC TANK - 7/18
"> <" indicates values not used in calculations

Date                    toluene           ethylene       trans-2-butene    isopentane     propane           propylene
                          area     conc.    area   conc.       area  conc.   area  conc.       area  conc.   area  conc.
                                   10.92            3.73              7.03          9.18              7.61          8.48
Carle I
7/18- Cal with Airco standard

                          26.7                                 22.9     >   23.7 <NOT US    24.1            26.6
                          32.1                                 22.6         29.9            24.1            26.5
ave                       29.40                                22.75        29.90           24.10           26.55
Cal today ppmC/area       0.372 <NOT USED                      0.309        0.307           0.316           0.320
-----------------------------------------------------------------------------------------
ave Carle I ppmC/area     0.313

Carle II
7/18- Cal with Airco standard

                     >    18.2 <            5.55                                     >      15.1 <          11.8
                          15.4              5.15                                            11.5            11.9
                          15.2              5.53                                            10.5            11.6
                          15.8              6.04                                            11.8            11.9
ave                       15.47             5.57                                            11.27           11.80
Cal today ppmC/area       0.706             0.670                                           0.676           0.719
-----------------------------------------------------------------------------------------
ave Carle II ppmC/area    0.693

Carle III
7/18- Cal with Airco standard

                     >    4.17 < NOT USED                      1.92     >    3.94 <                  4.26 propane &
                          3.31                                 1.82          2.37                    4.27 propylene
                          3.26                                 1.82          2.41                    4.27
                          3.25                                 1.82          2.38                    4.27
                          3.27                                 1.97          2.40                    4.39
ave                       3.27                                 1.87          2.39                   4.292
Cal today ppmC/area      3.337 < NOT USED                     3.757         3.842                   3.750
```

```
-------------------------------------------------------------------------------------------------------
ave Carle III ppmC/are 3.783
-------------------------------------------------------------------------------------------------------
Date                   toluene              ethylene      trans-2-butene    isopentane     propane                propylene
                         area      conc.    area   conc.       area   conc.   area   conc.      area     conc.     area   conc.
                                   10.92            3.73                 7.03           9.18                7.61            8.48
Carle I
8/14- Cal with Airco standard

                         26.3
                         27.1                              20.6            27.2           21.5            24.5
ave                      26.70                             20.9            27.4           21.3            23.8
Cal today ppmC/area      0.409 < NOT USED                  20.75           27.30          21.40           24.15
-----------------------------------------------------       0.339           0.336          0.356           0.351
ave Carle I ppmC/area    0.345 --------------------------------------------------------------------------------

Carle II
8/14- Cal with Airco standard

                         13.5            4.7
                         13.9            4.62                                              9.58            10.5
ave                      13.70           4.66                                              9.31            10.3
Cal today ppmC/area      0.797           0.800                                             9.45            10.40
-------------------------------------------------------------------------------------    0.806           0.816
ave Carle II ppmC/area 0.805 ---------------------------------------------------------------------------

Carle III
8/14- Cal with Airco standard

                         3.29
                         3.26                              1.95            2.57                  4.65 propane &
ave                      3.28                              1.97            2.57                  4.63
Cal today ppmC/area      3.336                             1.96            2.57                  4.64
----------------------------------------------------      3.584           3.573                 3.469
ave Carle III ppmC/are 3.490 -------------------------------------------------------------------------
-------------------------------------------------------------------------------------------------------
```

```
Liquid Injection Cals same day!
---------------------------------------------------------------------------------------------------
SIGMA 10 AREA CALS
Date                  toluene              m-xylene        o-xylene              pentane               2-me-pentane        di&tri-me-pentane
                       area         conc.    area   conc.        area     conc.    area      conc.        area   conc.     area   conc.
                                    2.99            2.98                  2.66               2.99                3.16              5.98
Carle I
8/14- Cal with LIQUID standards

                       8.06                 8.39             7.46                8.82                 8.47              17
                       8.17                 7.82             6.8                 8.52                 8.3               17.1
                       8.06                 7.37             6.4                 8.51                 9.14              16.6
ave                    8.10                 7.86             6.89                8.62                 8.64              16.90
Cal today ppmC/area    0.369                0.379            0.387               0.347                0.366             0.354
---------------------------------------------------------------------------------------------------
ave Carle I ppmC/area  0.367        aro     0.378    par     0.356 NOTE ARO CALS HIGHER THAN PAR
                                                     P/A=    0.94
Carle II
8/14- Cal with LIQUID standards

                       4.42                 4.33             3.72
                       4.22                 4.6              4.06
ave                    4.32                 4.47             3.89
Cal today ppmC/area    0.692                0.667            0.685
---------------------------------------------------------------------------------------------------
ave Carle II ppmC/area 0.681

Carle III
8/14- Cal with LIQUID standards

                       0.989                0.917            0.797               0.812
                       0.983                0.931            0.800               0.787
                                            0.917            0.784               0.787
ave                    0.986                0.922            0.794               0.795
Cal today ppmC/area    3.030                3.230            3.355               3.757
---------------------------------------------------------------------------------------------------
ave Carle III ppmC/are 3.343 NOTE DIFFERENCE BETWEEN AROS AND ALKANE
std dev                0.2654
```

PEAK HEIGHT CALS

| Date | toluene ht in | conc. 2.99 | m-xylene ht in | conc. 2.98 | o-xylene ht in | conc. 2.66 | pentane ht in | conc. 2.99 | 2-me-pentane ht in | conc. 3.16 |
|---|---|---|---|---|---|---|---|---|---|---|
| Carle I<br>8/14- Cal with LIQUID standards | | | | | | | | | | |
| | 6.8 | | 3.4 | | 2.4 | | 8.4 | | 6 | |
| | 7 | | 3.4 | | 2.4 | | 8.4 | | 5.8 | |
| | 6.86 | | 3.3 | | 2.4 | | 8.36 | | 5.8 | |
| ave | 6.89 | | 3.37 | | 2.40 | | 8.39 | | 5.87 | |
| Cal today ppmC/in | 0.434 | | 0.884 | | 1.110 | | 0.356 | | 0.539 | |
| Carle II<br>8/14- Cal with LIQUID standards | | | | | | | | | | |
| | 6.1 | | 3.2 | | 2.3 | | | | | |
| | 6.1 | | 3.2 | | 2.3 | | | | | |
| ave | 6.10 | | 3.20 | | 2.30 | | | | | |
| Cal today ppmC/in | 0.490 | | 0.930 | | 1.158 | | | | | |
| Carle III<br>8/14- Cal with LIQUID standards | | | | | | | | | | |
| | 13.2 | | 7.3 | | 5.2 | | | | | |
| | 13.2 | | 7.3 | | 5.2 | | | | | |
| ave | 13.20 | | 7.30 | | 5.20 | | | | | |
| Cal today ppmC/in | 0.226 | | 0.408 | | 0.512 | | | | | |

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Low MW Hi Conc Tank - Determination of Concentration based on Airco Cals - analyzed same day
Date
                          octane          ethylene/ethanbutanes-butenes   isopentane      propane             propylene
Carle I                     area    conc.    area              area          area            area                area
7/18- AIRCO ave ppmC/a 0.313

                          288.60             35.50             274.90        56.50           66.00               66.90
                          300.10             38.10             277.10        56.80           67.00               67.30
ave                       294.35    92.08    36.80   11.51     276.00  86.34 56.65   17.72   66.50   20.80       67.10   20.99
Date
                          pentane         2-me-1,3-butadiene
Carle I                     area    conc.    area
7/18- AIRCO ave ppmC/a 0.313

                           63.80            132.40
                           63.80            133.90
ave                        63.80    19.96   133.15   41.65

Date
                          octane          ethylene         ethane           propane/allenepropylene
Carle II                    area    conc.    area               area           area            area
7/18- AIRCO ave ppmC/a 0.693

                          129.30             13.40             13.30         47.60           27.20
                                             13.30             14.40         47.10
ave                       129.30    89.56    13.35    9.25     13.85   9.59  47.35   32.80   27.20   18.84

Date
                          octane          1-butene         n-butane         cis-2-butene   trans-butene      1,3-butadiene
Carle III                   area    conc.    area               area          area            area              area
7/18- AIRCO ave ppmC/a 3.783

                           28.20              4.91              2.71          4.98            5.12              4.51
                           28.30              5.10              2.83          5.09            5.21              4.63
ave                        28.25   106.87     5.01   18.93      2.77  10.48   5.04   19.05    5.17   19.54      4.57   17.29
Date
                         isopentane        pentane         propane/proplene/allene
Carle III                   area    conc.    area               area
7/18- AIRCO ave ppmC/a 3.783

                            4.88              7.12             14.80
                            5.98              8.55             16.50
ave                         5.43    20.54     7.84   29.64     15.65  59.20
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 THE 7/13 HI TO LO CONC COMPARISON FOR LOMW  TANKS
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Low MW HI CONC Tank as source for cal for determination of LOMW LO CONC Cal Tank same day
Date                       octane            ethylene/ethanbutanes-butenes  isopentane    propane           propylene
7/13                         area     conc.   area              area              area          area              area
Carle I                               96.17          18.84               85.29          17.72          20.80          20.99
                          319.70
                          299.70                             261.30         59.00         53.70          62.00
ave                       309.70                             259.00         58.40         52.50          61.30
Cal Today ppmC/area         0.31 <???                        260.15         58.70         53.10          61.65
                                                               0.33          0.30          0.39 <NOT US   0.34
Date                      pentane            2-me-1,3-butadiene
7/13                         area     conc.   area
Carle I                               19.96          41.65
                           65.40              138.30
                           65.00              136.50
ave                        65.20              137.40
Cal Today ppmC/area        0.306                0.303

Carle I ave ppmC/area     0.315

Date                       octane            ethylene        ethane
7/13                         area     conc.   area                area           propane/allenepropylene
Carle II                              96.17            9.25                9.59     area         area
                                                                                          35.51          20.99
                          148.30 <NOT USED   13.20             13.70
                          132.30             12.50             13.30           48.90          28.40
ave                       132.30             12.85             13.50           45.30 <NOT US  30.20
Cal Today ppmC/area        0.727              0.720             0.711          48.90          29.30
                                                                               0.726          0.716
Carle II ave ppmC/area 0.720

Date                       octane            1-butene        n-butane          cis-2-butene  trans-butene     1.3-butadiene
7/13                         area     conc.   area              area              area          area             area
Carle III                             96.17          18.93             10.48          19.05          19.54          17.29
                           27.90              4.77
                           27.40              4.86              2.57           4.83          4.95           4.34
ave                        27.65              4.82              2.68           4.93          5.03           4.47
Cal Today ppmC/area         3.48 <NOT USED    3.93              2.63           4.88          4.99           4.41
                                                                3.99           3.90          3.92           3.92
Date                      isopentane         pentane         propane/proplene/allene
7/13                         area     conc.   area              area
Carle III                             17.72          19.96             56.50
                            4.43              4.78
                            4.51              4.95              14.40
ave                         4.47              4.87              14.60
Cal Today ppmC/area         3.96              4.10              14.50
                                                                 3.90
Carle III ave ppmC/are    3.95
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Low MW Lo Conc Tank - Determination of Concentration based on HI conc Low MW Cals - analyzed same day
Date                    octane          ethylene/ethanbutanes-butenes  isopentane     propane          propylene
                         area    conc.   area               area        area            area             area
Carle I
7/13- LMWHI ave ppmC/a 0.315

                        19.62                               17.27        3.88            4.31             4.41
                        19.78                               17.28        3.83            4.07             4.85
ave                     19.70     6.21   0.00     0.00      17.28  5.44  3.86     1.21   4.19     1.32    4.63   1.46
Date                    pentane          2-me-1,3-butadiene
                         area    conc.   area
Carle I
7/13- LMWHI ave ppmC/a 0.315

                         4.38            8.21
                         4.33
ave                      4.36     1.37   8.21     2.59

Date                    octane           ethylene         ethane             propane/allenepropylene
                         area    conc.   area               area        area            area
Carle II
7/13- LMWHI ave ppmC/a 0.720

                                         1.87               1.19         3.45            2.67

ave                      0.00     0.00   1.87     1.35      1.19   0.86  3.45     2.48   2.67     1.92


Date                    octane           1-butene         n-butane           cis-2-butene  trans-butene   1,3-butadiene
                         area    conc.   area               area        area            area             area
Carle III
7/13- LMWHI ave ppmC/a 3.954

                         1.81            0.33               0.18                                          0.30
                         1.99            0.33               0.18         0.33            0.34             0.30
ave                      1.90     7.51   0.33     1.30      0.18   0.72  0.33     1.32   0.34     1.36    0.30   1.18
Date                   isopentane        pentane          propane/proplene/allene
                         area    conc.   area               area
Carle III
7/13- LMWHI ave ppmC/a 3.954

                         0.31                               0.99
                         0.31                               0.99
ave                      0.31     1.22   0.00     0.00      0.99   3.91
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Low MW Tank [illegible] for cal for determination of HMW Cal Tank same day
Date                  octane            ethylene/ethanbutanes-butenes  isopentane    propane         propylene
5/30                    area      conc.   area              area          area          area            area
Carle I                           96.17           18.84             85.29        17.72          20.80           20.99
                      329.00
                      336.10               56.70          281.40        58.30         70.30        68.40
ave                   332.55               56.50          280.50        57.70         70.20        68.20
Cal Today ppmC/area     0.29               56.60          280.95        58.00         70.25        68.30
                                            0.33            0.30         0.31          0.30         0.31
Date                  pentane           2-me-1,3-butadiene
5/30                    area      conc.   area
Carle I                           19.96           41.65
                       65.10               131.90
                       65.20               131.80
ave                    65.15               131.85
Cal Today ppmC/area     0.306                0.316

Carle I ave ppmC/area  0.307

Date                  octane            ethylene        ethane               propane/allenepropylene
5/30                    area      conc.   area             area                area          area
Carle II                          96.17           9.25              9.59             35.51         20.99
                      129.70               12.80           13.40         48.10               28.80
                      129.70               12.60           13.20         40.70 <NOT US       26.50 <NOT USED
ave                   129.70               12.70           13.30         48.10               28.80
Cal Today ppmC/area     0.741               0.728           0.721         0.738               0.729

Carle II ave ppmC/area 0.732

Date                  octane            1-butene        n-butane             cis-2-butene  trans-butene    1,3-butadiene
5/30                    area      conc.   area             area                area          area            area
Carle III                         96.17           18.93             10.48            19.05          19.54         17.29
                       28.30               4.63
                       28.30               4.67             2.54          4.69          4.75          4.30
ave                    28.30               4.65             2.56          4.72          4.80          4.30
Cal Today ppmC/area     3.40 <NOT USED     4.07             2.55          4.71          4.78          4.30
                                                            4.11          4.05          4.09          4.02
```

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Date                   isopentane          pentane          propane/proplene/allene
5/30                      area     conc.    area                  area
Carle III                          17.72              19.96                  56.50
                          4.30              4.71              13.90
                          4.32              4.72              13.90
ave                       4.31              4.72              13.90
Cal Today ppmC/area       4.11              4.23               4.06

Carle III ave ppmC/are    4.09

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High MW Tank - Determination of Concentration based on Airco Cals - analyzed same day

Date                     toluene          ethylbenzene  m-xylene           o-xylene        1-pentene
                          area     conc.   area  conc.      area  conc.     area  conc.      area  conc.
Carle I
7/18- AIRCO ave ppmC/a   0.313

                         60.50             63.50            61.90           60.80           49.60

ave                      60.50    18.93    63.50  19.86     61.90  19.36    60.80  19.02    49.60  15.52

Date                     toluene          ethylbenzene  m-xylene           o-xylene                         benzene
                          area     conc.   area                area           area                             area
Carle II
7/18- AIRCO ave ppmC/a   0.693

                         26.40             25.80            29.60           27.00
                                                                                                          24.00
ave                      26.40    18.29    25.80  17.87     29.60  20.50    27.00  18.70
                                                                                                          24.00  16.62
Date                     toluene          ethylbenzene  m-xylene           o-xylene        1-pentene        benzene
                          area     conc.   area  conc.      area  conc.     area  conc.      area  conc.     area
Carle III
7/18- AIRCO ave ppmC/a   3.783

                          6.12              6.42             6.80            6.37             7.21           5.74

ave                       6.12    23.15     6.42  24.29      6.80  25.72     6.37  24.10      7.21  27.27    5.74  21.71
                                                                                                  NOT USED
```

```
Date                    isobutane          cyclohexane
                           area     conc.     area
Carle III
7/18- AIRCO ave ppmC/a  3.783

                          3.03              9.64

ave                       3.03     11.46    9.64   36.47

Date                     toluene           ethylbenzene  m-xylene              o-xylene          1-pentene
                           area     conc.     area  conc.       area   conc.     area  conc.       area  conc.
Carle I
8/14- AIRCO ave ppmC/a  0.345

                          54.84             59.31            57.65             55.37              44.68
                          55.94             61.65            60.26             58.22              44.88
ave                       55.39    19.14    60.48  20.89     58.96   20.37     56.80  19.62       44.78  15.47

Date                     toluene           ethylbenzene  m-xylene              o-xylene          acetylene         benzene
                           area     conc.     area              area              area               area             area
Carle II
8/14- AIRCO ave ppmC/a  0.805

                          24.42             25.19            30.66             25.87              20.61             23.00
                          24.63             25.77            31.12             26.31              21.70             23.10
ave                       24.53    19.74    25.48  20.51     30.89   24.86     26.09  21.00       21.16  17.03     23.05  18.55

Date                     toluene           ethylbenzene  m-xylene              o-xylene          1-pentene         benzene
                           area     conc.     area  conc.       area   conc.     area  conc.       area  conc.      area
Carle III
8/14- AIRCO ave ppmC/a  3.490

                          6.73              7.07             7.29              7.08               4.30              6.36
                          6.82              7.20             7.45              7.08               4.31              6.43
ave                       6.78     23.65    7.14   24.91     7.37    25.73     7.08   24.70       4.30   15.02      6.40  22.32
Date                    isobutane          cyclohexane
                           area     conc.     area
Carle III
8/14- AIRCO ave ppmC/a  3.490

                          3.37
                          3.38
ave                       3.37     11.77
Date                     toluene           ethylbenzene  m-xylene              o-xylene          1-pentene
                           area     conc.     area  conc.       area   conc.     area  conc.       area  conc.
```

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Carle I
8/14- LIQUID ave ppmC/ 0.367

                            54.84           59.31           57.65           55.37           44.68
                            55.94           61.65           60.26           58.22           44.88
ave                         55.39   20.32   60.48   22.19   58.96   21.63   56.80   20.84   44.78   16.43

Date                        toluene        ethylbenzene m-xylene           o-xylene        acetylene       benzene
                             area   conc.    area            area            area            area            area
Carle II
8/14- LIQUID ave ppmC/ 0.681

                            24.42           25.19           30.66           25.87           20.61           23.00
                            24.63           25.77           31.12           26.31           21.70           23.10
ave                         24.53   16.70   25.48   17.35   30.89   21.04   26.09   17.77   21.16   14.41   23.05   15.70

Date                        toluene        ethylbenzene m-xylene           o-xylene        1-pentene       benzene
                             area   conc.    area   conc.    area   conc.    area   conc.    area   conc.    area
Carle III
8/14- LIQUID ave ppmC/ 3.343

                            6.73            7.07            7.29            7.08            4.30            6.36
                            6.82            7.20            7.45            7.08            4.31            6.43
ave                         6.78    22.65   7.14    23.86   7.37    24.65   7.08    23.66   4.30    14.38   6.40    21.38
Date                        isobutane      cyclohexane
                             area   conc.    area
Carle III
8/14- LIQUID ave ppmC/ 3.343

                            3.37
                            3.38
ave                         3.37    11.27

Date                        toluene         m-xylene        o-xylene
                            ph x64  conc.  ph x64   conc.     ph in conc.
Carle I
8/14-LIQ av ppmC/in x4 0.434                0.88            1.11

attn correction                16

                            2.95            1.55            1.27
                            3.00            1.60            1.30
ave                         2.98    20.65   1.58    22.28   1.29    22.81
```

| Date | toluene<br>ph in | conc. | m-xylene<br>ph in | conc. | o-xylene<br>ph in | conc. |
|---|---|---|---|---|---|---|
| Carle II<br>8/14-LIQ av ppmC/in x4 | 0.490 | | 0.93 | | 1.16 | |
| attn correction | 16 | | | | | |
| | 2.47 | | 1.80 | | 1.22 | |
| | 2.50 | | | | 1.25 | |
| ave | 2.49 | 19.48 | 1.80 | 26.79 | 1.24 | 22.88 |

| Date | toluene<br>ph in | conc. | m-xylene<br>ph in | conc. | o-xylene<br>ph in | conc. |
|---|---|---|---|---|---|---|
| Carle III<br>8/14-LIQ av ppmC/in x4 | 0.226 | | 0.41 | | 0.51 | |
| attn correction | 16 | | | | | |
| | 5.72 | | 3.72 | | 2.80 | |
| | 5.62 | | 3.80 | | 2.85 | |
| ave | 5.67 | 20.54 | 3.76 | 24.53 | 2.83 | 23.15 |

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| Date | toluene<br>area | conc. | ethylbenzene<br>area | conc. | m-xylene<br>area | conc. | o-xylene<br>area | conc. | 1-pentene<br>area | conc. | acetylene<br>area | conc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Carle I<br>5/30- LMWHC ave ppmC/a | 0.307 | | | | | | | | | | | |
| | 66.80 | | 66.50 | | 38.20 | | NA | | 48.60 | | 42.80 | |
| | 66.71 | | 67.70 | | 42.00 | | NA | | 48.60 | | 43.70 | |
| ave | 66.76 | 20.50 | 67.10 | 20.61 | 40.10 | 12.31 | NA | NA | 48.60 | 14.93 | 43.25 | 13.28 |

| Date | isobutane<br>area | conc. |
|---|---|---|
| Carle I<br>5/30- LMWHC ave ppmC/a | 0.307 | |
| | 29.60 | |
| | 30.70 | |
| ave | 30.15 | 9.26 |

```
Date                       toluene          ethylbenzene  m-xylene            o-xylene           acetylene          benzene
                             area      conc.    area           area              area               area              area
Carle II
5/30- LMWHC ave ppmC/a 0.732

                            25.40           26.00         29.50              27.10
                            25.70           26.40         30.80              28.20              23.80              23.40
ave                         25.55     18.69 26.20  19.17  30.15      22.06   27.65    20.23     24.60              23.70
                                                                                                24.20     17.70    23.55   17.23
Date                       toluene          ethylbenzene  m-xylene            o-xylene           1-pentene          benzene
                             area      conc.    area conc.     area     conc.    area   conc.      area   conc.     area
Carle III
5/30- LMWHC ave ppmC/a 4.094

                             5.83            6.08          6.24               5.97               3.63
                             5.80            6.17          6.32               6.05               3.61               5.48
ave                          5.82      23.81 6.13  25.07   6.28      25.71    6.01    24.60      3.62     14.82     5.47
                                                                                                                    5.48    22.41
Date                      Isobutane         cyclohexane
                             area      conc.    area
Carle III
5/30- LMWHC ave ppmC/a 4.094

                             2.84            4.67
                             2.85            5.53
ave                          2.85      11.65 5.10  20.88


-------------------------------------------------------------------
                       Airco Tank
                                         OCS 112  UNC/
                       manuf.  UNC- Dave UNC- Camanuf.
ethylene                4.80        3.65    3.73   0.78
propylene               9.15        8.34    8.48   0.93
propane                 8.61        7.47    7.61   0.88
toluene                 9.94       10.72   10.92   1.10
trans-2-butene          6.92        6.91    7.03   1.02
isopentane              9.85        9.03    9.18   0.93

                                                   0.94
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                         Low MW Tank HC
                       HIGH CONC                           OCS 109
                    manuf.  UNC-Dave U-Dave/Spread/    Spread         Carle I        Carle II          Carle ICarle III
                                      manuf. manuf.     Sheet         -------        ---------         -------
ethylene              10.0     9.32    0.93   0.92       9.25                           9.25
ethane                10.0     9.84    0.98   0.96       9.59                           9.59 ______
propylene             21.9    20.70    0.95   0.96      20.99          20.99 ______    18.84       )
propane               21.8    20.50    0.94   0.95      20.80          20.80 sum   )   32.80 sum   )    59.20     58.1
allene                15.0    17.60    1.17   0.98      14.70 ______         ______)       ______)
1-butene              19.0    18.80    0.96   0.97      18.93       )                             (     18.93     18.9
butane                10.8    10.40    0.96   0.97      10.48       )                             (     10.48     10.4
cis-2-butene          20.0    18.90    0.95   0.95      19.05 sum   )  86.34                85.29       19.05     19.2
trans-2-butene        19.6    19.40    0.99   1.00      19.54       )                             (     19.54     19.3
1,3-butadiene         20.0    17.20    0.86   0.96      17.29 ______)                             (     17.29     17.6
isopentane            18.1    17.40    0.96   0.98      17.72          17.72                            20.54     17.5
pentane               20.0    19.70    0.99   1.00      19.96          19.96                            29.64     19.3
2-methyl-1,3-butadiene 17.1   41.40    2.42   2.44      41.65          41.65
octane               104.2   104.00    1.00   0.92      96.17          92.08           89.56           106.87

                  ave                  0.97   0.96

                        Low MW Tank
                      HIGH CONC                  LOW CONC                  OCS 111
                   manuf.   UNC-Spd   UNC/       THC          UNC  low/hi      UNC  low/hi   low/hi/              Carle II ph der
                                      manuf.  x 0.073        Dave           Spread          avg low/hi            5/30   7/13     avg
ethylene             10.0      9.25    0.92    0.675        0.634  0.069    0.629  0.068     0.99  -0.01    0.667  0.592   0.629
ethane               10.0      9.59    0.96    0.700        0.644  0.067    0.628  0.065     0.95  -0.05    0.610  0.645   0.628
propylene            21.9     20.99    0.96    1.532        1.350  0.064    1.458  0.069     1.01   0.01                   0.000
propane              21.8     20.80    0.95   ·1.519        1.310  0.063    1.320  0.063     0.93  -0.07                   0.000
allene               15.0     14.70    0.98    1.073        1.240  0.084    1.148  0.078     1.14   0.14                   0.000
1-butene             19.6     18.93    0.97    1.382        1.300  0.069    1.305  0.069     1.01   0.01                   0.000
butane               10.8     10.48    0.97    0.765        0.713  0.068    0.716  0.068     1.00    .00                   0.000
cis-2-butene         20.0     19.05    0.95    1.390        1.310  0.069    1.317  0.069     1.01   0.01                   0.000
trans-2-butene       19.6     19.54    1.00    1.426        1.350  0.069    1.356  0.069     1.01   0.01                   0.000
1,3-butadiene        20.0     17.29    0.86    1.262        1.180  0.068    1.184  0.068     1.00    .00                   0.000
isopentane           18.1     17.72    0.98    1.294        1.210  0.068    1.218  0.069     1.00    .00                   0.000
pentane              20.0     19.96    1.00    1.457        1.340  0.067    1.372  0.069     1.00    .00                   0.000
2-methyl-1,3-butadiene 17.1   41.65    2.44    3.041        2.520  0.061    2.586  0.062     0.91  -0.09                   0.000
octane              104.2     96.17    0.92    7.020        6.800  0.071    6.859  0.071     1.04   0.04                   0.000
                                                                                                   sd
not including 2-me-1,3-butadiene ave   0.96    0.073               0.068           0.069     1.00   0.05
-----------------------------------------------------------------
```

```
                High MW Tank
                                    Carle I                              Carle II                                 Carle III
                Sprd av    5/30    7/18  8/14-T    8/14-L    5/30     7/18  8/14-T    8/14-L    5/30     7/18  8/14-T  8/14-L
acetylene        15.49    13.28                              17.704
isobutane        11.08     9.26                                                                11.646    11.46   11.77   11.27
1-pentene        15.22    14.93    15.52   15.47    16.43                                      14.819            15.02   14.38
benzene*         19.49                                       17.228    16.62   18.55    15.70  22.413    21.71   22.32   21.38
toluene*         20.46    20.50    18.93   19.14    20.32    18.691    18.29   19.74    16.70  23.805    23.15   23.65   22.65
ethylbenzene*    21.38    20.61    19.86   20.89    22.19    19.167    17.87   20.51    17.35  25.074    24.29   24.91   23.86
m-xylene*        22.88    12.31    19.36   20.37    21.63    22.057    20.50   24.86    21.04  25.709    25.72   25.73   24.65
o-xylene*        21.29       NA    19.02   19.62    20.84    20.228    18.70   21.00    17.77  24.603    24.10   24.70   23.66
* AVE NOT USED

                                   ave/  Meas.
                manuf.     Dave  manuf.    ave   Carle I Carle ICarle III
toluene          21.10    20.40    0.96  20.22     20.65   19.48  20.54
m-xylene         22.30    23.50    1.05  23.41     22.28   26.79  24.53 *CARLE II M-XYLENE NOT USED
o-xylene         22.40    22.50    1.02  22.95     22.81   22.88  23.15


                Car IIIMeas. ave/Car III *
                  ave    Car III  ave res.
benzene*         21.96              20.00
toluene*         23.32     0.87
ethylbenzene*    24.53              22.34
m-xylene*        25.45     0.92
o-xylene*        24.27     0.95
                ave res    0.91

                High MW Tank
                               UNC RTI-DavSprd av OCS 108  Carle III
                manuf.  RTI-Dave  manuf.  manuf.  Sprd ave Mo's 83
acetylene        14.60     12.90    0.88    1.06    15.49
isobutane        12.00     11.30    0.94    0.92    11.08   12.20
1-pentene        15.20     14.60    0.96    1.00    15.22   15.50
benzene**        20.00     20.00    1.00    1.00    20.00   22.70
toluene*         21.10     20.40    0.97    0.96    20.22   23.90
ethylbenzene**   23.80     22.50    0.95    0.94    22.34   24.30
m-xylene*        22.30     23.50    1.05    1.05    23.41   25.30
o-xylene*        22.40     22.50    1.00    1.02    22.95   23.50
            ave:                    0.97    0.99
```

```
                        Dimethylpentane  n-Octane       Ethylene             n-Butane          cis-butene
                         area     conc.   area  conc.       area    conc.     area   conc.       area   conc.
Carle I cal 5/30         79.10           117.80              8.50             26.30               23.90
ppmC/area =              81.80           130.50              8.52             26.40               24.10
               0.3071  -------          -------        ----------           -------           ---------
                         80.45    24.71  124.15  38.13       8.51    2.61     26.35   8.09       24.00   7.37

                        isopentane       2-me-1-butene  propane              propylene
                         area     conc.   area  conc.       area    conc.     area   conc.
Carle I cal 5/30         41.40            39.90             19.40             18.20
ppmC/area =              41.60            40.40             19.70             18.40
               0.3071  -------          -------        ----------           -------
                         41.50    12.74   40.15  12.33      19.55    6.00     18.30   5.62


                                         n-Octane       Ethylene
Carle II cal 5/30                         area  conc.       area    conc.
ppmC/area =                               45.60              3.43
               0.7316                     48.80              3.43
                                         -------        ----------
                                          47.20  34.53       3.43    2.51

                                                        propane              propylene
Carle II cal 5/30                                           area    conc.     area   conc.
ppmC/area =                                                 5.98              6.06
               0.7316                                       6.00              6.02
                                                        ----------          -------
                                                            5.99    4.38      6.04   4.42


                                         n-Octane
                                          area  conc.                        n-Butane          cis-butene
Carle III cal 5/30                        10.40                               area   conc.       area   conc.
ppmC/area =                               11.20                               1.90                1.78
               4.0938                    -------                              1.89                1.77
                                          10.80  44.21                      -------           ---------
                                                                              1.90   7.76        1.78   7.27

                        isopentane       2-me-1-butene              propane/propylene
                         area     conc.   area  conc.                 area  conc.
Carle III cal 5/30       3.03             3.21                        2.85
ppmC/area =              3.01             3.22                        2.83
               4.0938  -------          -------                     -------
                         3.02     12.36   3.22  13.16                 2.84  11.63
```

```
                     manuf.    OCS #1   Car I Car II  Car III    AVG  84/man.d rstd  84/OCS  d rstd
dimethylpentane      28.700    19.190  24.706
n-octane             27.680    20.223  38.127 34.530          24.706    0.86   0.56    1.29   -2.51
ethylene              2.680     2.718   2.613  2.509   44.213 38.957    1.41  -3.75    1.93   -7.56 <not used
n-butane              8.000     7.979   8.092                  2.561    0.96  -0.19    0.94    0.22
cis-2-butene          6.800     8.000   7.370           7.758  7.925    0.99  -0.46    0.99   -0.18
isopentane           19.500    12.971  12.745           7.267  7.318    1.08  -1.14    0.91    0.44
2-me-1-butene        15.450    16.300  12.330          12.363 12.554    0.64   2.27    0.97    0.02
propane               6.060     6.119   6.004          13.162 12.746    0.82   0.85    0.78    1.49
propylene             5.430     6.120   5.620  4.382 <not used 6.004    0.99  -0.46    0.98   -0.08
propylene+propane     11.49    12.239  11.623  4.419 <not used 5.620    1.03  -0.81    0.92    0.42
                                                       11.626 11.625    1.01  -0.63    0.95    0.17

                                                          ave           0.93           0.97
                                                          std dev       0.13           0.13

propylene- RTI
                     N      X           Y    N*X    N*Y         EY       X2      Y2      XY          ploty
------------------------------------------------------------------------------------------------     -------
                     1      1       14.58      1  14.58  14.699452        1  212.57   14.58          14.58
                     1     26       14.82     26  14.82  14.696710      676  219.63  385.32          14.82
                     1     27       14.34     27  14.34  14.696601      729  205.63  387.18          14.34
                     1    104       14.94    104  14.94  14.688156    10816  223.20  1553.7          14.94
                     1    749       14.79    749  14.79  14.617417   561001  218.74  11077.          14.79
                     1   2078        14.4   2078  14.40  14.471662    4E+06  207.36  29923.           14.4
------------------------------------------------------------------------------------------------     -------
                     6                      2985  87.87               5E+06  1287.1  43341.

                                   YBAR:  14.645               sd:          SLOPE: -1.1E-04
                                   XBAR:   497.5                            INTER: 14.69956
                                                                            R2:    0.138438

ethylene- RTI
                     N      X           Y    N*X    N*Y         EY       X2      Y2      XY          ploty
------------------------------------------------------------------------------------------------     -------
                     1      1       19.40      1  19.40  19.558797        1  376.36    19.4           19.4
                     1     29       19.20     29  19.20  19.555677      841  368.64   556.8           19.2
                     1    106       19.80    106  19.80  19.547098    11236  392.04  2098.8           19.8
                     0    740       16.80      0   0.00  19.476456        0       0       0             NA
                     1   1180       20.00   1180  20.00  19.427431    1E+06     400   23600             20
                     1   2225       19.00   2225  19.00  19.310995    5E+06     361   42275             19
------------------------------------------------------------------------------------------------     -------
                     5                      3541   97.4               6E+06  1898.0   68550

                                   YBAR:   19.48               sd:          SLOPE: -1.1E-04
                                   XBAR:   708.2                            INTER: 19.55890
                                                                            R2:    0.069424
```

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Comparison of RTI Propane Cal tank with other Cal Tanks

June 11, 1985

Carle 1
   OCS #       Conc   Resp in      Atten  cal @ x4       dev   rel dev
     112       7.61    6.4912         16    0.2931    0.0044     1.47%
     109       20.8    2.2345        128    0.2909    0.0066     2.21%
     171      44.34     8.985         64    0.3084   -0.0110    -3.68%
                                          ---------
                                   ave =    0.2975
                                   std =    0.0078
                               rel std =     2.62%

Carle 2
   OCS #       Conc   Resp in      Atten  cal @ x4       dev   rel dev
     112       7.61    1.6905         16    1.1254    0.0147     1.29%
     171      44.34    4.7991         32    1.1549   -0.0147    -1.29%
                                          ---------
                                   ave =    1.1402
                                   std =    0.0147
                               rel std =     1.29%

Carle 3
   OCS #       Conc   Resp in      Atten  cal @ x4       dev   rel dev
     112      16.09    6.7239         64    0.1496    0.0029     1.90%
     167     14.645    2.9965        128    0.1527   -0.0003    -0.18%
     171      44.34    4.4672        256    0.1551   -0.0026    -1.72%
                                          ---------
                                   ave =    0.1525
                                   std =    0.0023
                               rel std =     1.49%


June 18, 1985

Carle 1
   OCS #       Conc   Resp in      Atten  cal @ x4       dev   rel dev
     112       7.61    6.1926         16    0.3072    0.0023     0.75%
     109       20.8    2.1525        128    0.3020    0.0076     2.44%
     171      44.34    4.3381        128    0.3194   -0.0099    -3.19%
                                          ---------
                                   ave =    0.3095
                                   std =    0.0073
                               rel std =     2.36%

Carle 2
   OCS #       Conc   Resp in      Atten  cal @ x4       dev   rel dev
     112       7.61    1.7863         16    1.0651    0.1073     9.15%
     171      44.34    4.3315         32    1.2796   -0.1073    -9.15%
                                          ---------
                                   ave =    1.1723
                                   std =    0.1073
                               rel std =     9.15%

Carle 3
   OCS #       Conc   Resp in      Atten  cal @ x4       dev   rel dev
     112      16.09    6.9501         64    0.1447    0.0018     1.26%
     167     14.645     3.132        128    0.1461    0.0004     0.29%
     171      44.34    4.6557        256    0.1488   -0.0023     1.55%
                                          ---------
                                   ave =    0.1465
                                   std =    0.0017
                               rel std =     1.16%

                                     with 6/18 Carle 2  without
                               ave =          3.01%          1.79%
                               std =          2.80%          0.59%
                               ave+ 2 sd      8.61%          2.97%
```

# C

# Official Calibration Sources

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                         OFFICIAL CALIBRATION SOURCES          17-Nov-1986
                                                               Page 1

  ID                              SER                                STATED  ACTUAL
 NUM    DESC         SDATE        NUM                                 CONC    CONC

   1  82HCCALMIX   1-Jul-1982  XA-1336     ETHYLENE                   2.680   2.718
   1  82HCCALMIX   1-Jul-1982  XA-1336     PROPYLENE                  5.430   6.124
   1  82HCCALMIX   1-Jul-1982  XA-1336     PROPANE                    6.060   6.119
   1  82HCCALMIX   1-Jul-1982  XA-1336     N-BUTANE                   8.000   7.979
   1  82HCCALMIX   1-Jul-1982  XA-1336     CIS-2-BUTENE               6.800   8.000
   1  82HCCALMIX   1-Jul-1982  XA-1336     ISOPENTANE                19.500  12.971
   1  82HCCALMIX   1-Jul-1982  XA-1336     2-METHYL-1-BUTENE         15.450  16.300
   1  82HCCALMIX   1-Jul-1982  XA-1336     2,4-DIMETHYLPENTANE       28.700  19.190
   1  82HCCALMIX   1-Jul-1982  XA-1336     N-OCTANE                  27.680  20.223
   2  83COCH4CAL   1-Jun-1983  CAL-7820    METHANE                    5.648   5.648
   2  83COCH4CAL   1-Jun-1983  CAL-7820    CO                         5.405   5.405
   2  83COCH4CAL   1-Jun-1983  CAL-7820    CH4ASTHC                   5.648   5.648
   3  NOH1CONC     1-Jul-1981  1743571     NO                        50.000  59.597
   4  82NOSPAN     3-Sep-1982  CC-15860    NO                         0.810   0.823
   5  ACETALINJ    5-Jul-1983  AA-015808   ACETALDEHYDE               1.000   1.000
   6  PE900CLMX4  18-Jul-1983  NA          2-METHYLPENTANE            1.000   1.000
   6  PE900CLMX4  18-Jul-1983  NA          2,3-DIMETHYLPENTANE        1.000   1.000
   6  PE900CLMX4  18-Jul-1983  NA          METHYLCYCLOHEXANE          1.000   1.000
   6  PE900CLMX4  18-Jul-1983  NA          TOLUENE                    1.000   1.000
   6  PE900CLMX4  18-Jul-1983  NA          ETHYLBENZENE               1.000   1.000
   6  PE900CLMX4  18-Jul-1983  NA          M-XYLENE                   1.000   1.000
   6  PE900CLMX4  18-Jul-1983  NA          N-PROPYLBENZENE            1.000   1.000
   6  PE900CLMX4  18-Jul-1983  NA          2,2,4-TRIMETHYLPENTA       1.000   1.000
                                           NE
   6  PE900CLMX4  18-Jul-1983  NA          TERT-BUTYLBENZENE          1.000   1.000
   6  PE900CLMX4  18-Jul-1983  NA          1,3,5-TRIMETHYLBENZE       1.000   1.000
                                           NE
   7  TOLUENEINJ  14-Jun-1983              TOLUENE                    0.785   0.785
   8  PE900CLMX5   1-Jul-1982              BENZENE                    1.000   0.000
   8  PE900CLMX5   1-Jul-1982              P-XYLENE                   1.000   0.000
   8  PE900CLMX5   1-Jul-1982              O-XYLENE                   1.000   0.000
   8  PE900CLMX5   1-Jul-1982              1,2,4-TRIMETHYLBENZE       1.000   0.000
                                           NE
   8  PE900CLMX5   1-Jul-1982              SEC-BUTYLBENZENE           1.000   0.000
   8  PE900CLMX5   1-Jul-1982              M-ETHYLTOLUENE             1.000   0.000
   8  PE900CLMX5   1-Jul-1982              ISOPROPYLBENZENE           1.000   0.000
   8  PE900CLMX5   1-Jul-1982              1,2,3-TRIMETHYLBENZE       1.000   0.000
                                           NE
   8  PE900CLMX5   1-Jul-1982              BUTYLBENZENE               1.000   0.000
   9  PROPAB1746  17-Jul-1983  T658663     PROPYLENE                  1.100   1.100
  10  tolueneinj  27-Jun-1983  na          TOLUENE                    0.801   0.801
  11  82NMHCMIX    1-Jul-1982  XA-1336     NMHCASTHC                 ******  ******
  12  TOLUENEINJ   9-Jul-1983  NA          TOLUENE                    0.561   0.561
  13  MXYLENEINJ   9-Jul-1983  NA          M-XYLENE                   0.562   0.562
  14  ACETALINJ    5-Jul-1983  NA          ACETALDEHYDE               1.000   1.000
  15  PROPIONINJ   5-Jul-1983  NA          PROPIONALDEHYDE            1.000   0.999
  16  PROPAB1746  21-Jul-1983  T658663     PROPYLENE                  1.097   1.097
  17  PROPAB1746  29-Jul-1983  T658663     PROPYLENE                  1.097   1.097
  18  PROPAB1746  29-Jul-1983  T658663     PROPYLENE                  1.097   1.097
  19  PROPAB1746  31-Jul-1983  T658663     PROPYLENE                  1.097   1.097
  20  PROPAB1746  13-Aug-1983  T658663     PROPYLENE                  1.097   1.097
  21  PROPAB1746  13-Aug-1983  T658663     PROPYLENE                  1.097   1.097
  22  TOLUENEINJ  18-Aug-1983  NA          TOLUENE                    0.795   0.795
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OFFICIAL CALIBRATION SOURCES

17-Nov-1986
Page 2

| ID NUM | DESC | SDATE | SER NUM | | STATED CONC | ACTUAL CONC |
|---|---|---|---|---|---|---|
| 23 | TOLUENEINJ | 18-Aug-1983 | NA | TOLUENE | 0.795 | 0.795 |
| 24 | TOLUENEINJ | 26-Aug-1983 | NA | TOLUENE | 0.788 | 0.788 |
| 25 | | | | | 0.000 | 0.000 |
| 26 | | | | | 0.000 | 0.000 |
| 27 | TOLUENEINJ | 22-Aug-1983 | NA | TOLUENE | 0.584 | 0.584 |
| 28 | MXYLENEINJ | 22-Aug-1983 | NA | M-XYLENE | 0.584 | 0.584 |
| 29 | TOLUENEINJ | 6-Oct-1983 | NA | TOLUENE | 0.381 | 0.381 |
| 30 | TOLUENEINJ | 6-Oct-1983 | NA | TOLUENE | 0.381 | 0.381 |
| 31 | 124TMBINJB | 6-Oct-1983 | NA | 1,2,4-TRIMETHYLBENZENE | 0.233 | 0.233 |
| 32 | 124TMBINJR | 6-Oct-1983 | NA | 1,2,4-TRIMETHYLBENZENE | 0.233 | 0.233 |
| 33 | MXYLENEINJ | 6-Oct-1983 | NA | M-XYLENE | 0.180 | 0.180 |
| 34 | MXYLENEINJ | 6-Oct-1983 | NA | M-XYLENE | 0.180 | 0.180 |
| 35 | OXYLENEINJ | 6-Oct-1983 | NA | O-XYLENE | 0.111 | 0.111 |
| 36 | OXYLENEINJ | 6-Oct-1983 | NA | O-XYLENE | 0.111 | 0.111 |
| 37 | PE900CLMX4 | 23-Jul-1983 | NA | 2-METHYLPENTANE | 1.000 | 1.000 |
| 37 | PE900CLMX4 | 23-Jul-1983 | NA | 2,3-DIMETHYLPENTANE | 1.000 | 1.000 |
| 37 | PE900CLMX4 | 23-Jul-1983 | NA | METHYLCYCLOHEXANE | 1.000 | 1.000 |
| 37 | PE900CLMX4 | 23-Jul-1983 | NA | TOLUENE | 1.000 | 1.000 |
| 37 | PE900CLMX4 | 23-Jul-1983 | NA | ETHYLBENZENE | 1.000 | 1.000 |
| 37 | PE900CLMX4 | 23-Jul-1983 | NA | M-XYLENE | 1.000 | 1.000 |
| 37 | PE900CLMX4 | 23-Jul-1983 | NA | N-PROPYLBENZENE | 1.000 | 1.000 |
| 37 | PE900CLMX4 | 23-Jul-1983 | NA | 2,2,4-TRIMETHYLPENTANE | 1.000 | 1.000 |
| 37 | PE9[illegible]CLMX4 | 23-Jul-1983 | NA | TERT-BUTYLBENZENE | 1.000 | 1.000 |
| 37 | PE9[illegible]CLMX4 | 23-Jul-1983 | NA | 1,3,5-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 38 | TOLUENEINJ | 25-Jul-1983 | NA | TOLUENE | 0.601 | 0.601 |
| 39 | ISOPENTINJ | 25-Jul-1983 | NA | ISOPENTANE | 0.166 | 0.166 |
| 40 | 124TMBINJ | 25-Jul-1983 | NA | 1,2,4-TRIMETHYLBENZENE | 0.369 | 0.369 |
| 41 | TOLUENEINJ | 25-Jul-1983 | NA | TOLUENE | 0.601 | 0.601 |
| 42 | ISOPENTINJ | 25-Jul-1983 | NA | ISOPENTANE | 0.166 | 0.166 |
| 43 | 124TMBINJ | 25-Jul-1983 | NA | 1,2,4-TRIMETHYLBENZENE | 0.369 | 0.369 |
| 44 | TOLUENEINJ | 8-Aug-1983 | NA | TOLUENE | 9.125 | 9.125 |
| 45 | OXYLENEINJ | 8-Aug-1983 | NA | O-XYLENE | 6.083 | 6.083 |
| 46 | METOLINJ | 9-Aug-1983 | NA | M-ETHYLTOLUENE | 4.000 | 4.000 |
| 47 | 224TMPINJ | 19-Aug-1983 | NA | 2,2,4-TRIMETHYLPENTANE | 4.053 | 4.053 |
| 48 | ISOPENINJ | 19-Aug-1983 | NA | ISOPENTANE | 4.059 | 4.059 |
| 49 | OXYLENEINJ | 1-Aug-1983 | NA | O-XYLENE | 2.699 | 2.699 |
| 50 | TOLUENEINJ | 1-Aug-1983 | NA | TOLUENE | 4.553 | 4.529 |
| 51 | DETHKETINJ | 20-Jun-1983 | NA | 3-PENTANONE | 1.010 | 1.010 |
| 52 | DETHKETINJ | 20-Jun-1983 | NA | 3-PENTANONE | 1.010 | 1.010 |
| 53 | PE900CLMXS | 9-Sep-1983 | | BENZENE | 1.000 | 1.000 |
| 53 | PE900CLMXS | 9-Sep-1983 | | P-XYLENE | 1.000 | 1.000 |
| 53 | PE900CLMXS | 9-Sep-1983 | | O-XYLENE | 1.000 | 1.000 |
| 53 | PE900CLMXS | 9-Sep-1983 | | 1,2,4-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 53 | PE900CLMXS | 9-Sep-1983 | | SEC-BUTYLBENZENE | 1.000 | 1.000 |
| 53 | PE900CLMXS | 9-Sep-1983 | | M-ETHYLTOLUENE | 1.000 | 1.000 |

OFFICIAL CALIBRATION SOURCES

17-Nov-1986
Page 3

| ID NUM | DESC | SDATE | SER NUM | | STATED CONC | ACTUAL CONC |
|---|---|---|---|---|---|---|
| 53 | PE900CLMXS | 9-Sep-1983 | | ISOPROPYLBENZENE | 1.000 | 1.000 |
| 53 | PE900CLMXS | 9-Sep-1983 | | 1,2,3-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 53 | PE900CLMXS | 9-Sep-1983 | | BUTYLBENZENE | 1.000 | 1.000 |
| 54 | NEW83COCH4 | 30-Sep-1983 | | METHANE | 4.934 | 4.934 |
| 54 | NEW83COCH4 | 30-Sep-1983 | | CO | 5.114 | 5.114 |
| 55 | PE900CLMXS | 3-Oct-1983 | | BENZENE | 1.000 | 1.000 |
| 55 | PE900CLMXS | 3-Oct-1983 | | P-XYLENE | 1.000 | 1.000 |
| 55 | PE900CLMXS | 3-Oct-1983 | | O-XYLENE | 1.000 | 1.000 |
| 55 | PE900CLMXS | 3-Oct-1983 | | 1,2,4-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 55 | PE900CLMXS | 3-Oct-1983 | | SEC-BUTYLBENZENE | 1.000 | 1.000 |
| 55 | PE900CLMXS | 3-Oct-1983 | | M-ETHYLTOLUENE | 1.000 | 1.000 |
| 55 | PE900CLMXS | 3-Oct-1983 | | ISOPROPYLBENZENE | 1.000 | 1.000 |
| 55 | PE900CLMXS | 3-Oct-1983 | | 1,2,3-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 55 | PE900CLMXS | 3-Oct-1983 | | BUTYLBENZENE | 1.000 | 1.000 |
| 56 | PE900CLMXS | 4-Sep-1983 | | BENZENE | 1.000 | 1.000 |
| 56 | PE900CLMXS | 4-Sep-1983 | | P-XYLENE | 1.000 | 1.000 |
| 56 | PE900CLMXS | 4-Sep-1983 | | O-XYLENE | 1.000 | 1.000 |
| 56 | PE900CLMXS | 4-Sep-1983 | | 1,2,4-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 56 | PE900CLMXS | 4-Sep-1983 | | SEC-BUTYLBENZENE | 1.000 | 1.000 |
| 56 | PE900CLMXS | 4-Sep-1983 | | M-ETHYLTOLUENE | 1.000 | 1.000 |
| 56 | PE900CLMXS | 4-Sep-1983 | | ISOPROPYLBENZENE | 1.000 | 1.000 |
| 56 | PE900CLMXS | 4-Sep-1983 | | 1,2,3-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 56 | PE900CLMXS | 4-Sep-1983 | | BUTYLBENZENE | 1.000 | 1.000 |
| 57 | PE900CLMXS | 24-Jun-1983 | | BENZENE | 1.000 | 1.000 |
| 57 | PE900CLMXS | 24-Jun-1983 | | P-XYLENE | 1.000 | 1.000 |
| 57 | PE900CLMXS | 24-Jun-1983 | | O-XYLENE | 1.000 | 1.000 |
| 57 | PE900CLMXS | 24-Jun-1983 | | 1,2,4-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 57 | PE900CLMXS | 24-Jun-1983 | | SEC-BUTYLBENZENE | 1.000 | 1.000 |
| 57 | PE900CLMXS | 24-Jun-1983 | | M-ETHYLTOLUENE | 1.000 | 1.000 |
| 57 | PE900CLMXS | 24-Jun-1983 | | ISOPROPYLBENZENE | 1.000 | 1.000 |
| 57 | PE900CLMXS | 24-Jun-1983 | | 1,2,3-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 57 | PE90CLMXS | 24-Jun-1983 | | BUTYLBENZENE | 1.000 | 1.000 |
| 58 | PE900CLMXS | 30-Jun-1983 | | BENZENE | 1.000 | 1.000 |
| 58 | PE900CLMXS | 30-Jun-1983 | | P-XYLENE | 1.000 | 1.000 |
| 58 | PE900CLMXS | 30-Jun-1983 | | O-XYLENE | 1.000 | 1.000 |
| 58 | PE900CLMXS | 30-Jun-1983 | | 1,2,4-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 58 | PE900CLMXS | 30-Jun-1983 | | SEC-BUTYLBENZENE | 1.000 | 1.000 |
| 58 | PE900CLMXS | 30-Jun-1983 | | M-ETHYLTOLUENE | 1.000 | 1.000 |
| 58 | PE900CLMXS | 30-Jun-1983 | | ISOPROPYLBENZENE | 1.000 | 1.000 |
| 58 | PE900CLMXS | 30-Jun-1983 | | 1,2,3-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 58 | PE900CLMXS | 30-Jun-1983 | | BUTYLBENZENE | 1.000 | 1.000 |
| 59 | PE900CLMX4 | 3-Jun-1983 | | 2-METHYLPENTANE | 1.000 | 1.000 |
| 59 | PE900CLMXS | 3-Jun-1983 | | 2,3-DIMETHYLPENTANE | 1.000 | 1.000 |
| 59 | PE900CLMXS | 3-Jun-1983 | | METHYLCYCLOHEXANE | 1.000 | 1.000 |

OFFICIAL CALIBRATION SOURCES

17-Nov-1986
Page 4

| ID NUM | DESC | SDATE | SER NUM | | STATED CONC | ACTUAL CONC |
|---|---|---|---|---|---|---|
| 59 | PE900CLMXS | 3-Jun-1983 | | TOLUENE | 1.000 | 1.000 |
| 59 | PE900CLMXS | 3-Jun-1983 | | ETHYLBENZENE | 1.000 | 1.000 |
| 59 | PE900CLMXS | 3-Jun-1983 | | M-XYLENE | 1.000 | 1.000 |
| 59 | PE900CLMXS | 3-Jun-1983 | | N-PROPYLBENZENE | 1.000 | 1.000 |
| 59 | PE900CLMXS | 3-Jun-1983 | | 2,2,4-TRIMETHYLPENTANE | 1.000 | 1.000 |
| 59 | PE900CLMXS | 3-Jun-1983 | | TERT-BUTYLBENZENE | 1.000 | 1.000 |
| 59 | PE900CLMXS | 3-Jun-1983 | | 1,3,5-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 60 | PE900CLMXS | 6-Jul-1983 | NA | BENZENE | | 1.000 |
| 60 | PE900CLMXS | 6-Jul-1983 | NA | P-XYLENE | | 1.000 |
| 60 | PE900CLMXS | 6-Jul-1983 | NA | O-XYLENE | | 1.000 |
| 60 | PE900CLMXS | 6-Jul-1983 | NA | 1,2,4-TRIMETHYLBENZENE | | 1.000 |
| 60 | PE900CLMXS | 6-Jul-1983 | NA | SEC-BUTYLBENZENE | | 1.000 |
| 60 | PE900CLMXS | 6-Jul-1983 | NA | M-ETHYLTOLUENE | | 1.000 |
| 60 | PE900CLMXS | 6-Jul-1983 | NA | ISOPROPYLBENZENE | | 1.000 |
| 60 | PE900CLMXS | 6-Jul-1983 | NA | 1,2,3-TRIMETHYLBENZENE | | 1.000 |
| 60 | PE900CLMXS | 6-Jul-1983 | NA | BUTYLBENZENE | | 1.000 |
| 61 | PE900CLMX5 | 18-Jul-1983 | NA | BENZENE | 1.000 | 1.000 |
| 61 | PE900CLMX5 | 18-Jul-1983 | NA | P-XYLENE | 1.000 | 1.000 |
| 61 | PE900CLMX5 | 18-Jul-1983 | NA | O-XYLENE | 1.000 | 1.000 |
| 61 | PE900CLMX5 | 18-Jul-1983 | NA | 1,2,4-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 61 | PE900CLMX5 | 18-Jul-1983 | NA | SEC-BUTYLBENZENE | 1.000 | 1.000 |
| 61 | PE900CLMX5 | 18-Jul-1983 | NA | M-ETHYLTOLUENE | 1.000 | 1.000 |
| 61 | PE900CLMX5 | 18-Jul-1983 | NA | ISOPROPYLBENZENE | 1.000 | 1.000 |
| 61 | PE900CLMX5 | 18-Jul-1983 | NA | 1,2,3-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 61 | PE900CLMX5 | 18-Jul-1983 | NA | BUTYLBENZENE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | 2-METHYLPENTANE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | 2,3-DIMETHYLPENTANE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | METHYLCYCLOHEXANE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | TOLUENE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | ETHYLBENZENE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | M-XYLENE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | N-PROPYLBENZENE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | 2,2,4-TRIMETHYLPENTANE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | TERT-BUTYLBENZENE | 1.000 | 1.000 |
| 62 | PE900CLMX4 | 18-Jul-1983 | | 1,3,5-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 63 | PE900CLMX5 | 23-Jul-1983 | | BENZENE | 1.000 | 1.000 |
| 63 | PE900CLMX5 | 23-Jul-1983 | | P-XYLENE | 1.000 | 1.000 |
| 63 | PE900CLMX5 | 23-Jul-1983 | | O-XYLENE | 1.000 | 1.000 |
| 63 | PE900CLMX5 | 23-Jul-1983 | | 1,2,4-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 63 | PE900CLMX5 | 23-Jul-1983 | | SEC-BUTYLBENZENE | 1.000 | 1.000 |
| 63 | PE900CLMX5 | 23-Jul-1983 | | M-ETHYLTOLUENE | 1.000 | 1.000 |
| 63 | PE900CLMX5 | 23-Jul-1983 | | ISOPROPYLBENZENE | 1.000 | 1.000 |
| 63 | PE900CLMX5 | 23-Jul-1983 | | 1,2,3-TRIMETHYLBENZENE | 1.000 | 1.000 |

OFFICIAL CALIBRATION SOURCES

17-Nov-1986
Page 5

| ID NUM | DESC | SDATE | SER NUM | | STATED CONC | ACTUAL CONC |
|---|---|---|---|---|---|---|
| 63 | PE900CLMX5 | 23-Jul-1983 | | BUTYLBENZENE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | 2-METHYLPENTANE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | 2,3-DIMETHYLPENTANE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | METHYLCYCLOHEXANE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | TOLUENE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | ETHYLBENZENE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | M-XYLENE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | N-PROPYLBENZENE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | 2,2,4-TRIMETHYLPENTANE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | TERT-BUTYLBENZENE | 1.000 | 1.000 |
| 64 | PE900CLMX4 | 23-Jul-1983 | | 1,3,5-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 65 | PE900CLMX5 | 2-Aug-1983 | | BENZENE | 1.000 | 1.000 |
| 65 | PE900CLMX5 | 2-Aug-1983 | | P-XYLENE | 1.000 | 1.000 |
| 65 | PE900CLMX5 | 2-Aug-1983 | | O-XYLENE | 1.000 | 1.000 |
| 65 | PE900CLMX5 | 2-Aug-1983 | | 1,2,4-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 65 | PE900CLMX5 | 2-Aug-1983 | | SEC-BUTYLBENZENE | 1.000 | 1.000 |
| 65 | PE900CLMX5 | 2-Aug-1983 | | M-ETHYLTOLUENE | 1.000 | 1.000 |
| 65 | PE900CLMX5 | 2-Aug-1983 | | ISOPROPYLBENZENE | 1.000 | 1.000 |
| 65 | PE900CLMX5 | 2-Aug-1983 | | 1,2,3-TRIMETHYLBENZENE | 1.000 | 1.000 |
| 65 | PE900CLMX5 | 2-Aug-1983 | | BUTYLBENZENE | 1.000 | 1.000 |
| 66 | HCOHINJ | 6-Jun-1983 | | FORMALDEHYDE | 1.072 | 1.072 |
| 67 | HCOHINJ | 15-Jun-1983 | | FORMALDEHYDE | 1.000 | 1.000 |
| 68 | HCOHINJ | 24-Nov-1983 | | FORMALDEHYDE | 1.024 | 1.024 |
| 69 | HCOHINJ | 18-Jun-1983 | | FORMALDEHYDE | 1.041 | 1.041 |
| 70 | HCOHINJ | 12-Jul-1983 | | FORMALDEHYDE | 1.029 | 1.029 |
| 71 | HCOHINJ | 12-Aug-1983 | | FORMALDEHYDE | 1.032 | 0.000 |
| 72 | HCOHINJ | 23-Jul-1983 | | FORMALDEHYDE | 1.047 | 1.047 |
| 73 | HCOHINJ | 29-Jul-1983 | | FORMALDEHYDE | 1.026 | 1.026 |
| 74 | HCOHINJ | 13-Aug-1983 | | FORMALDEHYDE | 1.016 | 1.016 |
| 75 | HCOHINJ | 19-Sep-1983 | | FORMALDEHYDE | 1.026 | 1.026 |
| 76 | NO2ASPAN | 10-Jun-1983 | | PAN | 0.244 | 0.244 |
| 77 | NO2ASPAN | 18-Jun-1983 | | PAN | 0.152 | 0.152 |
| 78 | NO2ASPAN | 13-Jul-1983 | | PAN | 0.037 | 0.037 |
| 79 | NO2ASPAN | 17-Jul-1983 | | PAN | 0.071 | 0.071 |
| 80 | no2aspan | 18-Jul-1983 | | PAN | 0.055 | 0.055 |
| 81 | no2aspan | 20-Jul-1983 | | PAN | 0.081 | 0.081 |
| 82 | no2aspan | 21-Jul-1983 | | PAN | 0.061 | 0.061 |
| 83 | no2aspan | 26-Jul-1983 | | PAN | 0.025 | 0.025 |
| 84 | no2aspan | 29-Jul-1983 | | PAN | 0.074 | 0.074 |
| 85 | no2aspan | 31-Jul-1983 | | PAN | 0.059 | 0.059 |
| 86 | no2aspan | 4-Aug-1983 | | PAN | 0.036 | 0.036 |
| 87 | no2aspan | 13-Aug-1983 | | PAN | 0.074 | 0.074 |
| 88 | no2aspan | 5-Sep-1983 | | PAN | 0.105 | 0.105 |
| 89 | no2aspan | 7-Sep-1983 | | PAN | 0.096 | 0.096 |
| 90 | no2aspan | 18-Sep-1983 | | PAN | 0.114 | 0.114 |
| 91 | no2aspan | 23-Sep-1983 | | PAN | 0.100 | 0.100 |
| 92 | no2aspan | 2-Oct-1983 | | PAN | 0.200 | 0.200 |
| 93 | NO2ASPAN | 14-Oct-1983 | | PAN | 0.110 | 0.110 |
| 94 | NO46PPMCAL | 22-Jun-1934 | SX13759 | NO | 46.000 | 52.600 |

OFFICIAL CALIBRATION SOURCES

17-Nov-1986
Page 6

| ID NUM | DESC | SDATE | SER NUM | | STATED CONC | ACTUAL CONC |
|---|---|---|---|---|---|---|
| 95 | MXYLENEINJ | 25-Jun-1984 | | M-XYLENE | 3.000 | 2.968 |
| 96 | TOLUENEINJ | 25-Jun-1984 | | TOLUENE | 6.000 | 5.895 |
| 97 | TOLUENE | 27-Jun-1984 | | TOLUENE | 5.000 | 4.909 |
| 98 | M-XYLENE | 26-Jun-1984 | | M-XYLENE | 3.000 | 2.978 |
| 99 | O-XYLENE | 26-Jun-1984 | | O-XYLENE | 3.000 | 2.653 |
| 100 | TOLUENE | 19-Jun-1984 | | TOLUENE | 4.000 | 3.929 |
| 101 | M-XYLENE | 19-Jun-1984 | | M-XYLENE | 3.000 | 2.967 |
| 102 | FORMALDEHY | 10-Jul-1984 | | FORMALDEHYDE | 0.500 | 0.542 |
| 103 | FORMALDEHY | 10-Jul-1984 | | FORMALDEHYDE | 1.060 | 1.035 |
| 104 | HCHOINJB | 11-Jul-1984 | NA | FORMALDEHYDE | 1.000 | 0.946 |
| 105 | HCHOINJR | 11-Jul-1984 | NA | FORMALDEHYDE | 1.000 | 0.946 |
| 106 | HCHOINJRAF | 27-Jul-1984 | NA | FORMALDEHYDE | 1.000 | 0.946 |
| 107 | HCHOINJRMO | 27-Jul-1984 | NA | FORMALDEHYDE | 0.200 | 0.189 |
| 108 | HIMWHICONC | | | ACETYLENE | 14.600 | 15.490 |
| 108 | HIMWHICONC | | | ISOBUTANE | 12.000 | 11.080 |
| 108 | HIMWHICONC | | | 1-PENTENE | 15.175 | 15.200 |
| 108 | HIMWHICONC | | | BENZENE | 19.956 | 19.910 |
| 108 | HIMWHICONC | | | TOLUENE | 21.056 | 20.300 |
| 108 | HIMWHICONC | | | ETHYLBENZENE | 23.784 | 22.250 |
| 108 | HIMWHICONC | | | M-XYLENE | 22.272 | 23.590 |
| 108 | HIMWHICONC | | | O-XYLENE | 22.432 | 22.950 |
| 109 | LOMWHICONC | | | ETHYLENE | 10.004 | 9.250 |
| 109 | LOMWHICONC | | | ETHANE | 10.000 | 9.590 |
| 109 | LOMWHICONC | | | PROPYLENE | 21.906 | 20.990 |
| 109 | LOMWHICONC | | | PROPANE | 21.894 | 20.800 |
| 109 | LOMWHICONC | | | PROPADIENE | 15.000 | 14.700 |
| 109 | LOMWHICONC | | | 1-BUTENE | 19.600 | 18.930 |
| 109 | LOMWHICONC | | | N-BUTANE | 10.800 | 10.480 |
| 109 | LOMWHICONC | | | 1,3-BUTADIENE | 20.000 | 17.290 |
| 109 | LOMWHICONC | | | TRANS-2-BUTENE | 20.000 | 19.540 |
| 109 | LOMWHICONC | | | CIS-2-BUTENE | 20.000 | 19.050 |
| 109 | LOMWHICONC | | | ISOPENTANE | 18.135 | 17.720 |
| 109 | LOMWHICONC | | | N-PENTANE | 19.956 | 19.960 |
| 109 | LOMWHICONC | | | N-OCTANE | ****** | 96.170 |
| 109 | LOMWHICONC | | | 2-METHYL-1,3-BUTADIENE | 17.055 | 41.650 |
| 110 | SCOTT84 | | | ETHYLENE | 0.600 | 0.711 |
| 110 | SCOTT84 | | | PROPYLENE | 0.900 | 1.128 |
| 110 | SCOTT84 | | | PROPANE | 0.900 | 0.972 |
| 110 | SCOTT84 | | | CIS-2-BUTENE | 1.000 | 1.110 |
| 110 | SCOTT84 | | | ISOPENTANE | 1.250 | 1.145 |
| 110 | SCOTT84 | | | N-PENTANE | 1.250 | 1.347 |
| 110 | SCOTT84 | | | TOLUENE | 2.800 | 3.250 |
| 110 | SCOTT84 | | | 2-METHYL-2-BUTENE | 1.250 | 1.390 |
| 111 | LOMWLOCONC | | | ETHYLENE | 0.000 | 0.629 |
| 111 | LOMWLOCONC | | | ETHANE | 0.000 | 0.628 |
| 111 | LOMWLOCONC | | | PROPYLENE | 0.000 | 1.458 |
| 111 | LOMWLOCONC | | | PROPANE | 0.000 | 1.320 |
| 111 | LOMWLOCONC | | | PROPADIENE | 0.000 | 1.148 |
| 111 | LOMWLOCONC | | | 1-BUTENE | 0.000 | 1.305 |
| 111 | LOMWLOCONC | | | N-BUTANE | 0.000 | 0.716 |
| 111 | LOMWLOCONC | | | 1,3-BUTADIENE | 0.000 | 1.184 |
| 111 | LOMWLOCONC | | | TRANS-2-BUTENE | 0.000 | 1.356 |

OFFICIAL CALIBRATION SOURCES 17-Nov-1986
Page 7

| ID NUM | DESC | SDATE | SER NUM | | STATED CONC | ACTUAL CONC |
|---|---|---|---|---|---|---|
| 111 | LOMWLOCONC | | | CIS-2-BUTENE | 0.000 | 1.317 |
| 111 | LOMWLOCONC | | | ISOPENTANE | 0.000 | 1.218 |
| 111 | LOMWLOCONC | | | N-PENTANE | 0.000 | 1.372 |
| 111 | LOMWLOCONC | | | N-OCTANE | 0.000 | 6.859 |
| 111 | LOMWLOCONC | | | 2-METHYL-1,3-BUTADIENE | 0.000 | 2.586 |
| 112 | NEWAIRCO84 | | | ETHYLENE | 4.800 | 3.730 |
| 112 | NEWAIRCO84 | | | PROPYLENE | 9.150 | 8.480 |
| 112 | NEWAIRCO84 | | | PROPANE | 8.610 | 7.610 |
| 112 | NEWAIRCO84 | | | TRANS-2-BUTENE | 6.920 | 7.030 |
| 112 | NEWAIRCO84 | | | ISOPENTANE | 9.850 | 9.180 |
| 112 | NEWAIRCO84 | | | TOLUENE | 9.940 | 10.920 |
| 112 | NEWAIRCO84 | | | PROPYLENE/PROPANE | 17.760 | 16.090 |
| 113 | PROPYL741 | | N415664 | PROPYLENE | 7.410 | 7.410 |
| 114 | TOLUENE211 | | | TOLUENE | 14.770 | 14.770 |
| 115 | HCHOINJ | 31-Jul-1984 | NA | FORMALDEHYDE | 1.000 | 0.946 |
| 116 | TOLUENEINJ | 28-Jun-1984 | NA | TOLUENE | 6.000 | 5.977 |
| 117 | MXYLENEINJ | 28-Jun-1984 | NA | M-XYLENE | 3.000 | 3.009 |
| 118 | AROMINJ | 16-Jul-1984 | NA | BENZENE | 2.000 | 2.000 |
| 118 | AROMINJ | 16-Jul-1984 | NA | TOLUENE | 2.000 | 2.000 |
| 118 | AROMINJ | 16-Jul-1984 | NA | P-XYLENE | 2.000 | 2.000 |
| 118 | AROMINJ | 16-Jul-1984 | NA | M-XYLENE | 2.000 | 2.000 |
| 118 | AROMINJ | 16-Jul-1984 | NA | O-XYLENE | 2.000 | 2.000 |
| 118 | AROMINJ | 16-Jul-1984 | NA | STYRENE | 2.000 | 2.000 |
| 119 | TMPENTINJ | 27-Jul-1985 | NA | 2,2,4-TRIMETHYLPENTANE | 1.000 | 1.000 |
| 120 | BENZENEINJ | 27-Jul-1984 | NA | BENZENE | 1.000 | 1.000 |
| 121 | RTIETHYL | | | ETHYLENE | 19.000 | 19.480 |
| 122 | RTIPROPYL | | | PROPYLENE | 14.400 | 14.650 |
| 123 | HIMWLIQINJ | 14-Aug-1984 | DFB | N-PENTANE | 3.000 | 2.988 |
| 123 | HIMWLIQINJ | 14-Aug-1984 | DFB | 2-METHYLPENTANE | 3.000 | 3.161 |
| 123 | HIMWLIQINJ | 14-Aug-1984 | DFB | 2,3-DIMETHYLPENTANE | 3.000 | 2.990 |
| 123 | HIMWLIQINJ | 14-Aug-1984 | DFB | TOLUENE | 3.000 | 2.988 |
| 123 | HIMWLIQINJ | 14-Aug-1984 | DFB | M-XYLENE | 3.000 | 2.976 |
| 123 | HIMWLIQINJ | 14-Aug-1984 | DFB | O-XYLENE | 2.600 | 2.663 |
| 123 | HIMWLIQINJ | 14-Aug-1984 | DFB | 2,2,4-TRIMETHYLPENTANE | 3.000 | 2.992 |
| 124 | M-XYLENE | 27-Jun-1984 | LMQ | M-XYLENE | 2.000 | 1.978 |
| 125 | HCHOINJ | 13-Jul-1984 | LMQ | FORMALDEHYDE | 1.000 | 1.038 |
| 126 | HCHOINJ | 13-Jul-1984 | LMQ | FORMALDEHYDE | 1.000 | 1.038 |
| 127 | MEOHINJ | 24-Jul-1984 | JBS | METHANOL | 0.900 | 0.891 |
| 128 | MEOHINJ | 3-Aug-1984 | DFB | METHANOL | 0.900 | 0.897 |
| 129 | MEOHINJ | 4-Aug-1984 | JRA | METHANOL | 0.300 | 0.321 |
| 130 | MEOHINJ | 7-Aug-1984 | DFB | METHANOL | 0.300 | 0.300 |
| 131 | MEOHINJ | 8-Aug-1984 | JRA | METHANOL | 0.790 | 0.787 |
| 132 | MEOHINJ | 9-Aug-1984 | LMQ | METHANOL | 0.263 | 0.263 |
| 133 | HCHOINJ | 7-Oct-1984 | NA | FORMALDEHYDE | 1.000 | 0.918 |
| 134 | HCHOINJ | 7-Oct-1984 | NA | FORMALDEHYDE | 0.500 | 0.464 |
| 135 | HCHOINJ | 9-Oct-1984 | NA | FORMALDEHYDE | 1.000 | 0.920 |
| 136 | HCHOINJ | 9-Oct-1984 | NA | FORMALDEHYDE | 1.000 | 0.920 |
| 137 | HCHOINJ | 16-Oct-1984 | NA | FORMALDEHYDE | 0.250 | 0.232 |
| 138 | HCHOINJ | 16-Oct-1984 | NA | FORMALDEHYDE | 0.500 | 0.465 |
| 139 | 85COCH4CAL | 3-Apr-1985 | AAL-15140 | METHANE | 1.907 | 1.907 |

## OFFICIAL CALIBRATION SOURCES

17-Nov-1986
Page 8

| ID NUM | DESC | SDATE | SER NUM | | STATED CONC | ACTUAL CONC |
|---|---|---|---|---|---|---|
| 139 | 85COCH4CAL | 3-Apr-1985 | AAL-15140 | CO | 3.950 | 3.950 |
| 140 | MEOHINJ | 25-Aug-1984 | | METHANOL | 0.300 | 0.292 |
| 141 | ACETALDINJ | 27-Aug-1984 | | ACETALDEHYDE | 1.000 | 1.000 |
| 142 | ACETALDINJ | 27-Aug-1984 | | ACETALDEHYDE | 1.000 | 1.000 |
| 143 | MEOHINJ | 1-Sep-1984 | JRA | METHANOL | 1.000 | 0.970 |
| 144 | MEOHINJ | 3-Sep-1984 | KCS | METHANOL | 0.266 | 0.264 |
| 145 | ACETALDINJ | 16-Sep-1984 | KGS | ACETALDEHYDE | 1.000 | 1.000 |
| 146 | ACETALDINJ | 16-Sep-1984 | KGS | ACETALDEHYDE | 1.000 | 1.000 |
| 147 | MEOHINJ | 17-Sep-1984 | LMQ | METHANOL | 0.600 | 0.572 |
| 148 | HCHOINJ | 25-Sep-1984 | DFB | FORMALDEHYDE | 1.000 | 0.932 |
| 149 | NO2ASPAN | 20-Aug-1984 | NA | PAN | 0.160 | 0.160 |
| 150 | NO2ASPAN | 20-Aug-1984 | NA | PAN | 0.153 | 0.153 |
| 151 | NO2ASPAN | 18-Sep-1984 | NA | PAN | 0.191 | 0.191 |
| 152 | NO2ASPAN | 18-Sep-1984 | NA | PAN | 0.131 | 0.131 |
| 153 | NO2ASPAN | 3-Oct-1984 | NA | PAN | 0.166 | 0.166 |
| 154 | NO2ASPAN | 3-Oct-1984 | NA | PAN | 0.165 | 0.165 |
| 155 | NO2ASPAN | 4-Oct-1984 | NA | PAN | 0.164 | 0.164 |
| 156 | NO2ASPAN | 11-Oct-1984 | NA | PAN | 0.166 | 0.166 |
| 157 | NO2ASPAN | 30-Aug-1984 | NA | PAN | 0.169 | 0.169 |
| 158 | NO2ASPAN | 6-Jul-1984 | NA | PAN | 0.207 | 0.207 |
| 159 | HCHOINJ | 5-Sep-1985 | NA | FORMALDEHYDE | 1.000 | 0.961 |
| 160 | ACETINJ | 15-Oct-1984 | NA | ACETALDEHYDE | 1.000 | 1.000 |
| 161 | ACETINJ | 15-Oct-1984 | NA | ACETALDEHYDE | 1.000 | 1.000 |
| 162 | AROMINJ | 14-May-1985 | NA | BENZENE | 0.500 | 0.450 |
| 162 | AROMINJ | 14-May-1985 | NA | TOLUENE | 1.000 | 1.005 |
| 162 | AROMINJ | 14-May-1985 | NA | M-XYLENE | 2.000 | 1.999 |
| 162 | AROMINJ | 14-May-1985 | NA | 2,2,4-TRIMETHYLPENTANE | 2.000 | 1.929 |
| 163 | AROMINJ | 17-May-1985 | NA | BENZENE | 0.500 | 0.545 |
| 163 | AROMINJ | 17-May-1985 | NA | TOLUENE | 1.000 | 1.064 |
| 163 | AROMINJ | 17-May-1985 | NA | M-XYLENE | 2.000 | 2.105 |
| 163 | AROMINJ | 17-May-1985 | NA | 2,2,4-TRIMETHYLPENTANE | 3.000 | 2.349 |
| 164 | HCHOINJ | 20-May-1985 | NA | FORMALDEHYDE | 1.000 | 1.046 |
| 165 | AROMINJ | 22-May-1985 | NA | BENZENE | 1.500 | 1.659 |
| 165 | AROMINJ | 22-May-1985 | NA | TOLUENE | 2.000 | 2.161 |
| 165 | AROMINJ | 22-May-1985 | NA | M-XYLENE | 4.000 | 4.274 |
| 165 | AROMINJ | 22-May-1985 | NA | O-XYLENE | 5.000 | 5.543 |
| 165 | AROMINJ | 22-May-1985 | NA | 1,2,4-TRIMETHYLBENZENE | 5.000 | 5.379 |
| 165 | AORMINJ | 22-May-1985 | NA | 2,2,4-TRIMETHYLPENTANE | 1.000 | 0.795 |
| 166 | | | | | 0.000 | 0.000 |
| 166 | AROMINJ | 24-May-1985 | NA | BENZENE | 1.500 | 1.613 |
| 166 | AROMINJ | 24-May-1985 | NA | TOLUENE | 2.000 | 2.101 |
| 166 | AROMINJ | 24-May-1985 | NA | M-XYLENE | 4.000 | 4.155 |
| 166 | AROMINJ | 24-May-1985 | NA | O-XYLENE | 5.000 | 5.389 |
| 166 | AROMINJ | 24-May-1985 | NA | 2,2,4-TRIMETHYLPENTANE | 1.000 | 0.773 |
| 167 | RTIPROPYLE | 3-Jun-1985 | NA | PROPYLENE | 14.400 | 14.645 |
| 168 | RTIETHYLEN | 3-Jun-1985 | NA | ETHYLENE | 19.000 | 19.480 |
| 171 | RTI PROPAN | 11-Jun-1985 | NA | PROPANE | 14.780 | 14.780 |
| 173 | HCHOINJB | 21-Jun-1985 | JRA | FORMALDEHYDE | 0.750 | 0.738 |

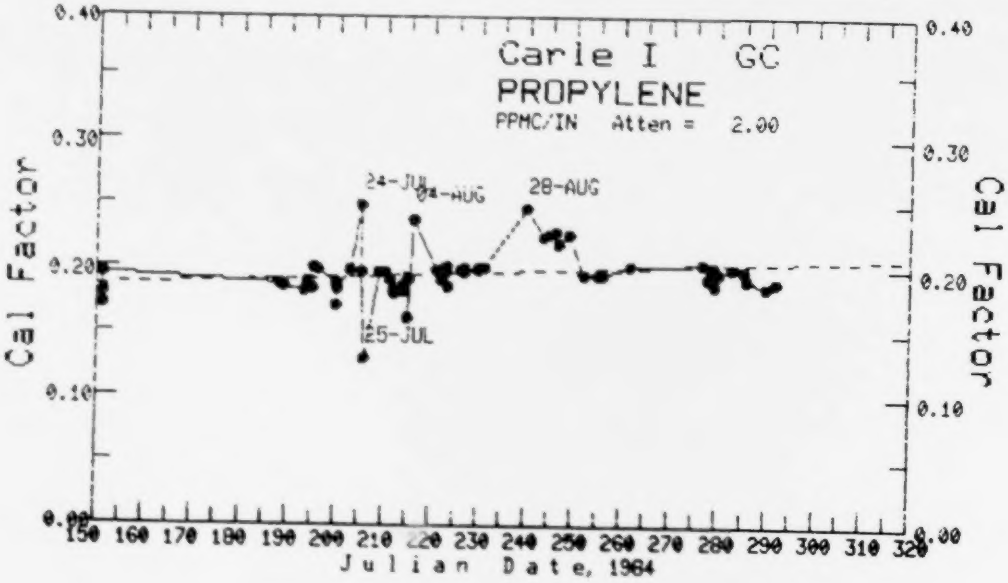
## OFFICIAL CALIBRATION SOURCES

17-Nov-1986
Page 9

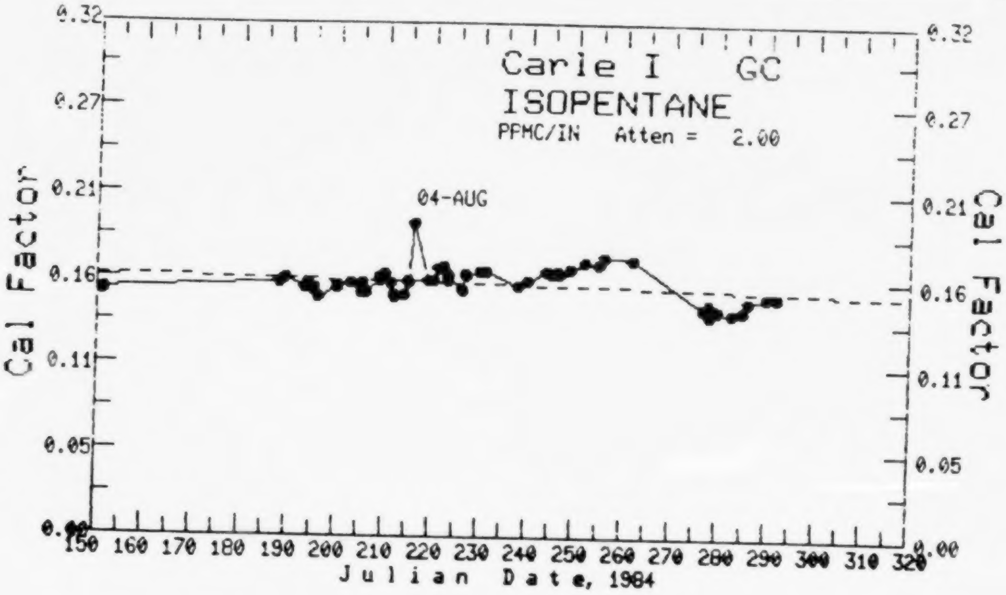
| ID NUM | DESC | SDATE | SER NUM | | STATED CONC | ACTUAL CONC |
|---|---|---|---|---|---|---|
| 174 | HCHOINJR | 21-Jun-1985 | JRA | FORMALDEHYDE | 1.500 | 1.470 |
| 175 | HCHOPERM85 | 31-Aug-1982 | 96-17902 | FORMALDEHYDE | 0.189 | 0.189 |
| 176 | HCHOINJR | 8-Aug-1985 | JRA | FORMALDEHYDE | 1.000 | 0.993 |
| 177 | LIQAROMINJ | 8-Aug-1985 | JLS | BENZENE | 1.500 | 1.669 |
| 177 | LIQAROMINJ | 8-Aug-1985 | JRA | TOLUENE | 2.000 | 2.173 |
| 177 | LIQAROMINJ | 8-Aug-1985 | JRA | M-XYLENE | 4.000 | 4.298 |
| 177 | LIQAROMINJ | 8-Aug-1985 | JRA | O-XYLENE | 5.000 | 5.574 |
| 177 | LIQAROMINJ | 8-Aug-1985 | JRA | 1,2,4-TRIMETHYLBENZENE | 5.000 | 5.409 |
| 177 | LIQAROMINJ | 8-Aug-1985 | JRA | 2,2,4-TRIMETHYLPENTANE | 1.000 | 0.799 |
| 178 | AIRCONO | | 1122590 | NO | 52.400 | 52.458 |
| 179 | SCOTTNO | | BAL177 | NO | 52.600 | 52.600 |
| 180 | LOWNOAUTO | | | NO | 0.000 | 0.288 |
| 181 | LOWNOAUTO2 | | | NO | 0.693 | 0.665 |
| 182 | LMWHCONTHC | | | THC | ****** | ****** |
| 183 | AIRCO84THC | | | THC | 67.030 | 62.960 |
| 186 | LIQAROMINJ | 26-Aug-1986 | JOHN | BENZENE | 1.500 | 1.659 |
| 186 | LIQAROMINJ | 26-Aug-1985 | JOHN | TOLUENE | 2.000 | 2.161 |
| 186 | LIQAROMINJ | 26-Aug-1985 | JOHN | M-XYLENE | 4.000 | 4.274 |
| 186 | LIQAROMINJ | 26-Aug-1985 | JOHN | O-XYLENE | 5.000 | 5.543 |
| 186 | LIQAROMINJ | 26-Aug-1985 | JOHN | 1,2,4-TRIMETHYLBENZENE | 5.000 | 5.379 |
| 186 | LIQAROMINJ | 26-Aug-1985 | JOHN | 2,2,4-TRIMETHYLPENTANE | 0.800 | 0.795 |
| 187 | HCHOINJB | 12-Sep-1985 | JOHN | FORMALDEHYDE | 1.000 | 1.018 |
| 188 | HCHOINJR | 12-Sep-1985 | JOHN | FORMALDEHYDE | 0.500 | 0.496 |
| 189 | HCHOINJ | 30-Sep-1985 | JOHN | FORMALDEHYDE | 1.000 | 0.993 |
| 190 | TOL LIQINJ | 29-Aug-1985 | | TOLUENE | 0.750 | 0.730 |
| 191 | M-XYL INJ | 29-Aug-1985 | | M-XYLENE | 0.750 | 0.734 |
| 192 | 124TMB INJ | 15-Aug-1985 | | 1,2,4-TRIMETHYLBENZENE | 0.900 | 0.905 |
| 193 | M-XYL INJ | 15-Aug-1985 | | M-XYLENE | 0.900 | 0.899 |
| 194 | M-XYL INJ | 12-Aug-1985 | | M-XYLENE | 0.900 | 0.906 |
| 195 | 124TMB INJ | 12-Aug-1985 | | 1,2,4-TRIMETHYLBENZENE | 0.900 | 0.904 |

# D

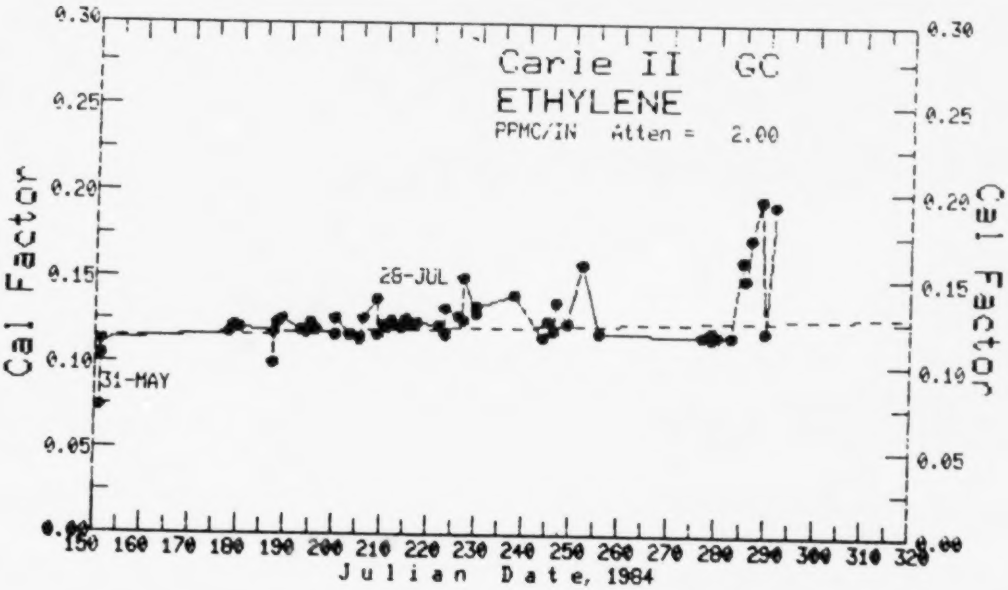
# CALANA Plots and Reports



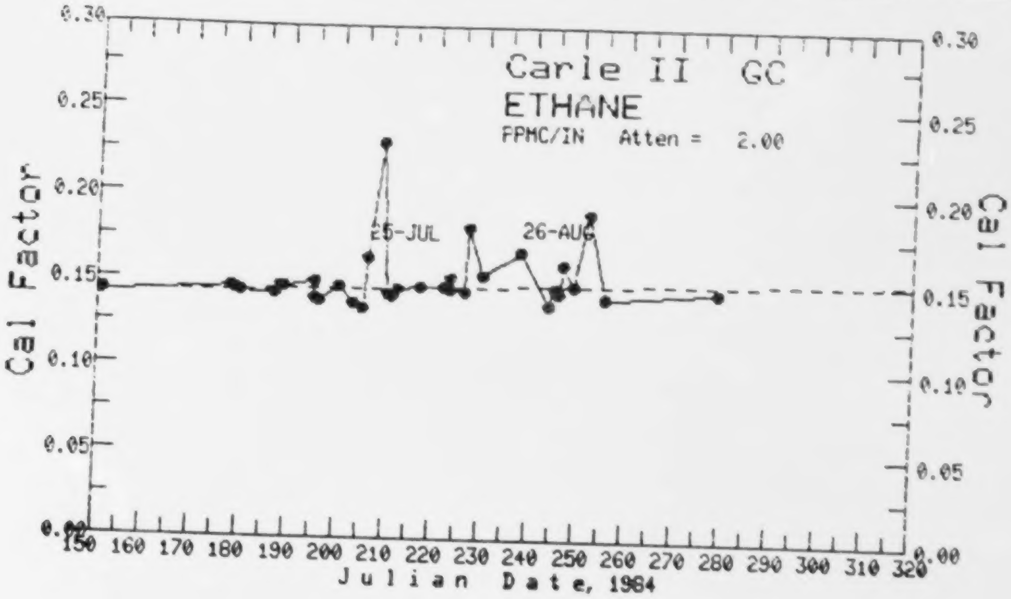
```
For the species PROPYLENE and the instrument Carle I   GC:

Beginning Caldate:             30-MAY-84
                    Day:       150
Ending    Caldate:             16-NOV-84
                    Day:       320
Upper CalFactor Limit             0.40000
Lower CalFactor Limit             0.00000

The number of data points         62
The number included  was          62
The slope of this fit  is 1.3522654E-004
       with a std dev of 6.6911662E-005   rel. dev = 49.5 %
The intercept is          1.6694184E-001
       with a std dev of 1.5341250E-002   rel. dev = 9.2 %
The std dev of the fit is 1.8079919E-002   FE =  0.01205
The correlation coeff is    0.25246

The min, mean, max are       0.13040,    0.19760,    0.25009
The standard deviation is  0.01853   rel. dev = 9.4 %

Cal =  0.00014 X (Julian Date - 150) +  0.18723

                        ...press RETURN-key when ready...
```



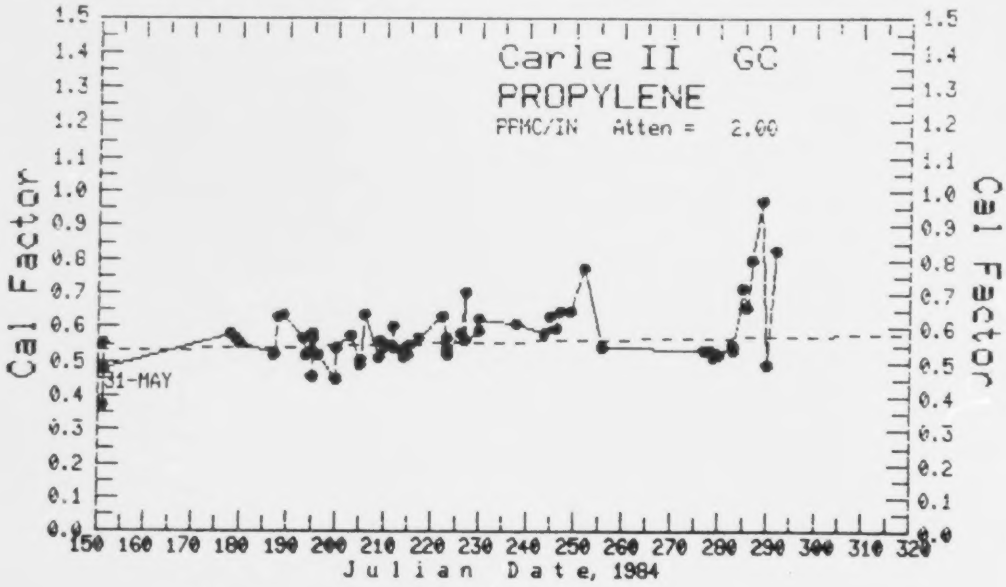
```
For the species ISOPENTANE and the instrument Carle I   GC:

Beginning Caldate:            30-MAY-84
                    Day:      150
Ending    Caldate:            16-NOV-84
                    Day:      320
Upper CalFactor Limit            0.32000
Lower CalFactor Limit            0.00000

The number of data points        61
The number included  was         61
The slope of this fit  is -6.274875E-005
       with a std dev of  3.6480040E-005   rel. dev = -58.1 %
The intercept is          1.7246965E-001
       with a std dev of  8.4102093E-003   rel. dev = 4.9 %
The std dev of the fit is 9.7288922E-003   PE =  0.00649
The correlation coeff is  -0.21852

The min, mean, max are        0.13965,    0.15816,    0.19620
The standard deviation is  0.00989   rel. dev = 6.3 %

Cal = -0.00006 X (Julian Date - 150) +  0.16306
```



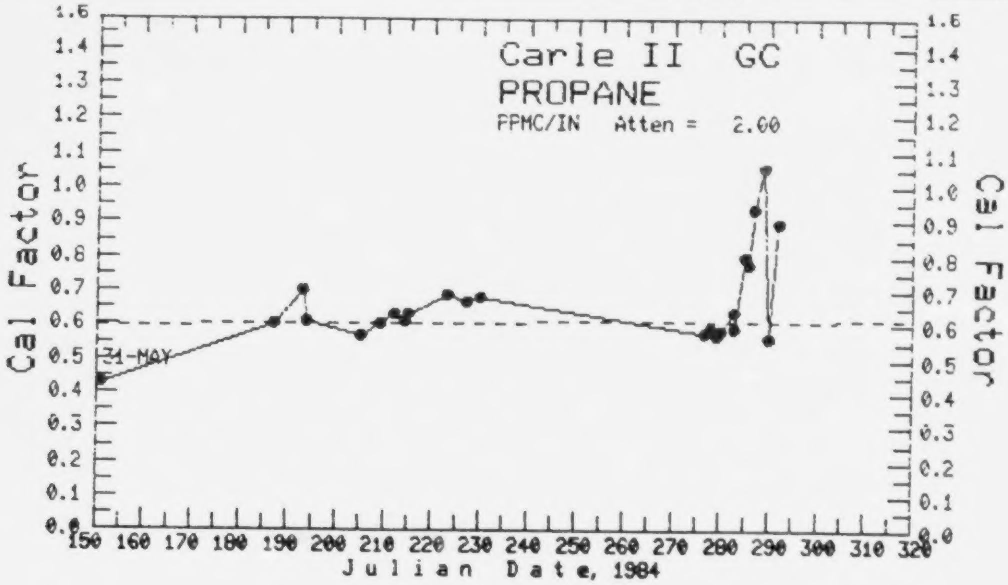
```
For the species ETHYLENE and the instrument Carle II  GC:

Beginning Caldate:              30-MAY-84
                     Day:       150
Ending     Caldate:             16-NOV-84
                     Day:       320
Upper CalFactor Limit              0.14000
Lower CalFactor Limit              0.00000

The number of data points        61
The number included  was         53
The slope of this fit  is 7.7424523E-005
       with a std dev of 3.6302085E-005    rel. dev = 46.9 %
The intercept is          1.0432247E-001
       with a std dev of 7.9898236E-003    rel. dev = 7.7 %
The std dev of the fit is 8.8857276E-003   PE =  0.00592
The correlation coeff is    0.28616

The min, mean, max are        0.07444,     0.12116,     0.19795
The standard deviation is  0.00918   rel. dev = 7.6 %

Cal =  0.00008 X (Julian Date - 150) +  0.11594

                      ...press RETURN-key when ready...
```



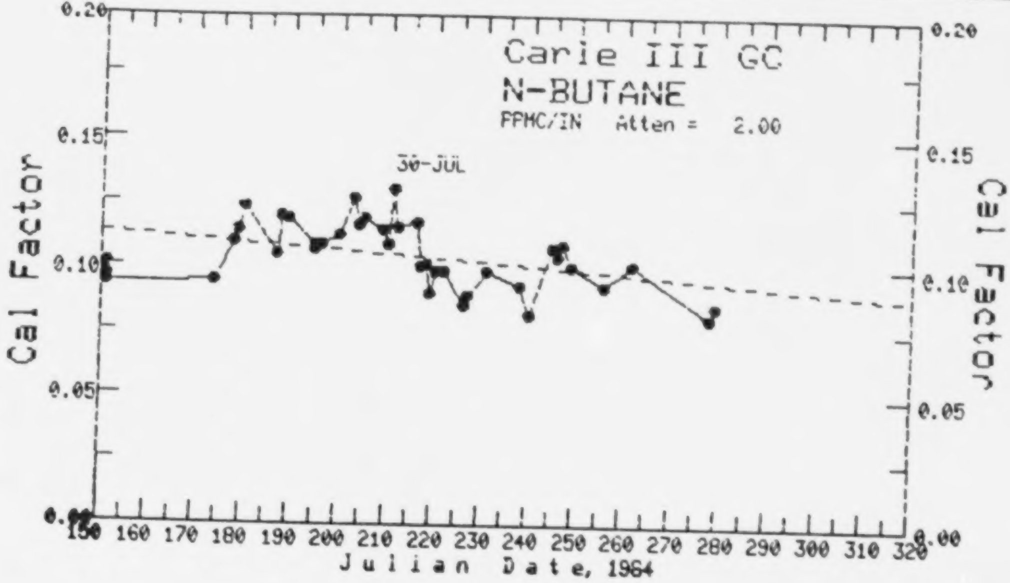
```
For the species ETHANE and the instrument Carle II  GC:

Beginning Caldate:                30-MAY-84
                          Day:    150
Ending     Caldate:               16-NOV-84
                          Day:    320
Upper CalFactor Limit                0.18000
Lower CalFactor Limit                0.00000

The number of data points          35
The number included  was           32
The slope of this fit  is 5.6237375E-005
       with a std dev of 4.3453789E-005    rel. dev = 77.3 %
The intercept is          1.3469188E-001
       with a std dev of 9.2956360E-003    rel. dev = 6.9 %
The std dev of the fit is 7.1982245E-003   PE =  0.00480
The correlation coeff is   0.22995

The min, mean, max are        0.13445,    0.14661,    0.23050
The standard deviation is  0.00728   rel. dev = 5.0 %

Cal =  0.00006 X (Julian Date - 150) +  0.14313
```



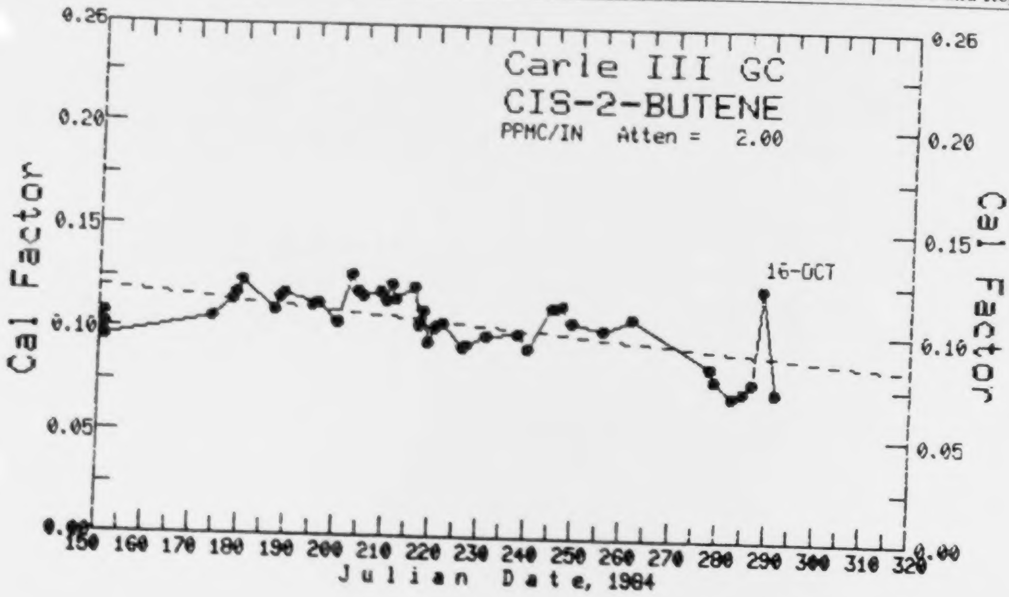
```
For the species PROPYLENE and the instrument Carle II  GC:

Beginning Caldate:            30-MAY-84
                     Day:     150
Ending     Caldate:           16-NOV-84
                     Day:     320
Upper CalFactor Limit           0.70000
Lower CalFactor Limit           0.00000

The number of data points       63
The number included   was       57
The slope of this fit  is 3.2677424E-004
       with a std dev of 2.0339685E-004    rel. dev = 62.2 %
The intercept is          4.8080472E-001
       with a std dev of 4.5272312E-002    rel. dev = 9.4 %
The std dev of the fit is 5.3626706E-002   PE =  0.03575
The correlation coeff is    0.21172

The min, mean, max are          0.36888,     0.55264,     0.97565
The standard deviation is   0.05438    rel. dev = 9.8 %

Cal =  0.00033 X (Julian Date - 150) +  0.52982

                         ...press RETURN-key when ready...
```



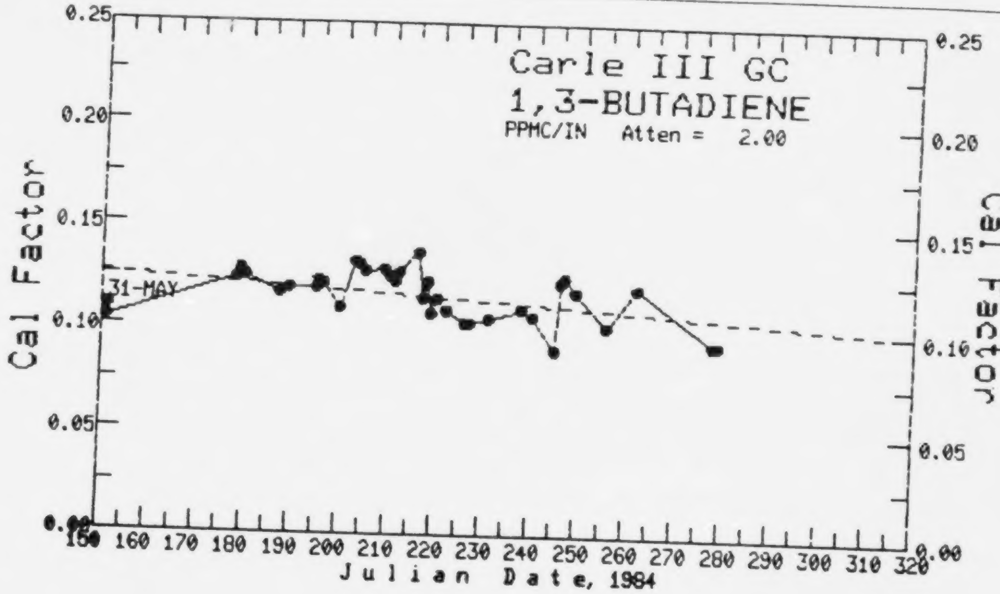
```
For the species PROPANE and the instrument Carle II  GC:

Beginning Caldate:           30-MAY-84
                       Day:  150
Ending     Caldate:          16-NOV-84
                       Day:  320
Upper CalFactor Limit          0.70000
Lower CalFactor Limit          0.00000

The number of data points      24
The number included  was       19
The slope of this fit  is 9.3254754E-005
       with a std dev of 3.4843816E-004    rel. dev = 373.6 %
The intercept is          5.8478932E-001
       with a std dev of 8.2456137E-002    rel. dev = 14.1 %
The std dev of the fit is 6.1473938E-002   PE =  0.04098
The correlation coeff is    0.06478

The min, mean, max are        0.42750,    0.60653,    1.05930
The standard deviation is  0.05987   rel. dev = 9.9 %

Cal =  0.00009 X (Julian Date - 150) +  0.59878
```



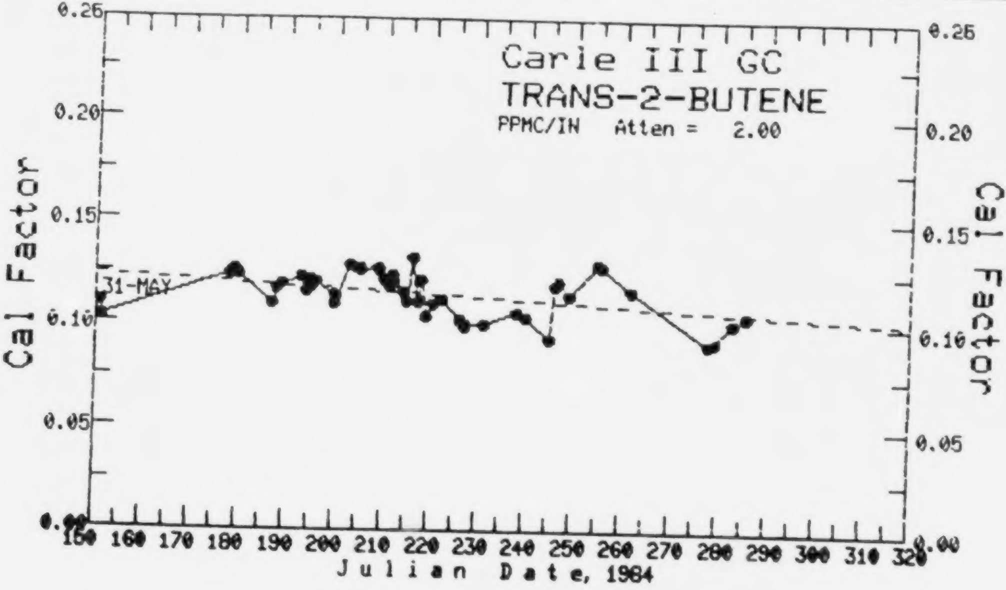
```
For the species N-BUTANE and the instrument Carle III GC:

Beginning Caldate:          30-MAY-84
                      Day:  150
Ending    Caldate:          16-NOV-84
                      Day:  320
Upper CalFactor Limit           0.20000
Lower CalFactor Limit           0.00000

The number of data points       40
The number included  was        40
The slope of this fit  is -1.501925E-004
       with a std dev of 5.7705246E-005   rel. dev = -38.4 %
The intercept is          1.3697557E-001
       with a std dev of 1.2401192E-002   rel. dev = 9.1 %
The std dev of the fit is 1.1458466E-002  PE =  0.00764
The correlation coeff is  -0.38897

The min, mean, max are        0.08147,    0.10504,    0.13079
The standard deviation is  0.01228   rel. dev = 11.7 %

Cal = -0.00015 X (Julian Date - 150) +  0.11445
```



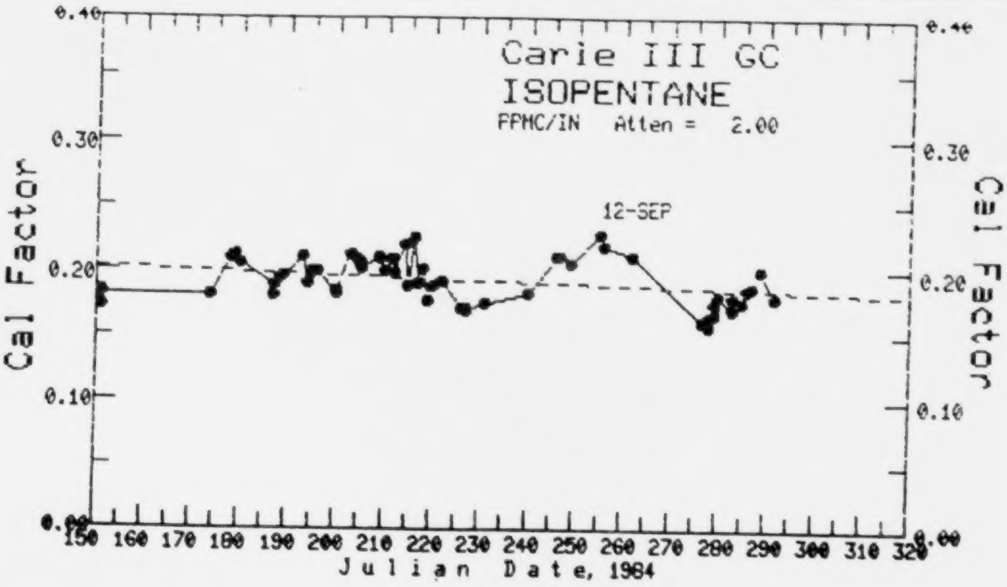
```
For the species CIS-2-BUTENE and the instrument Carle III GC:

Beginning Caldate:             30-MAY-84
                         Day:  150
Ending    Caldate:             16-NOV-84
                         Day:  320
Upper CalFactor Limit            0.35000
Lower CalFactor Limit            0.00000

The number of data points        45
The number included  was         45
The slope of this fit  is -2.188447E-004
        with a std dev of 4.8220399E-005    rel. dev = -22.0 %
The intercept is           1.5340966E-001
        with a std dev of 1.0805980E-002    rel. dev = 7.0 %
The std dev of the fit is 1.2219133E-002    PE =  0.00815
The correlation coeff is  -0.56910

The min, mean, max are         0.07010,     0.10507,     0.12707
The standard deviation is  0.01469    rel. dev = 14.0 %

Cal = -0.00022 X (Julian Date - 150) +  0.12058

                    ...press RETURN-key when ready...
```



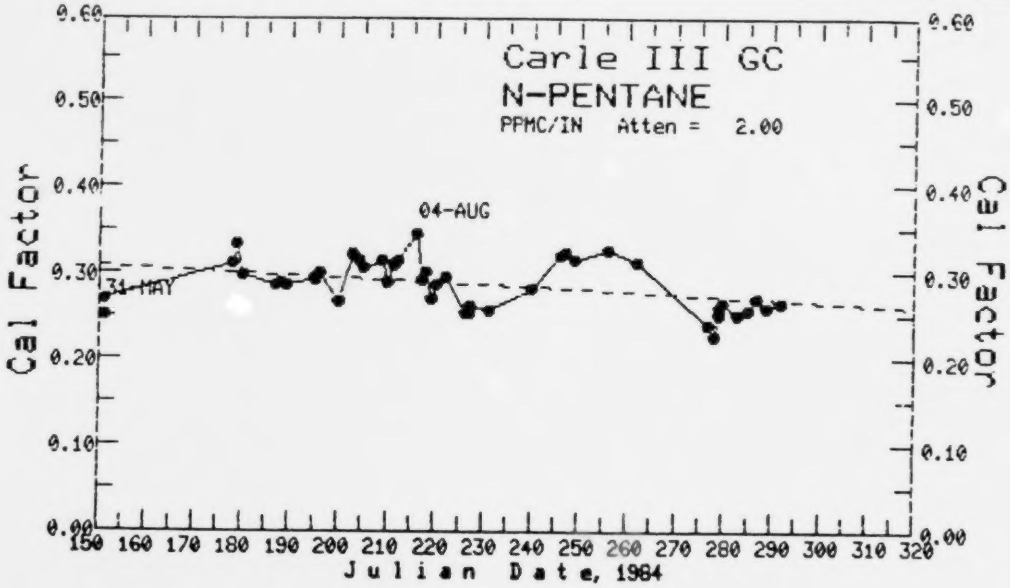
```
For the species 1,3-BUTADIENE and the instrument Carle III GC:

Beginning Caldate:            30-MAY-84
                      Day:    150
Ending    Caldate:            16-NOV-84
                      Day:    320
Upper CalFactor Limit            0.25000
Lower CalFactor Limit            0.00000

The number of data points        38
The number included  was         38
The slope of this fit  is -1.547570E-004
       with a std dev of 5.7985070E-005   rel. dev = -37.5 %
The intercept is          1.4937310E-001
       with a std dev of 1.2600050E-002   rel. dev = 8.4 %
The std dev of the fit is 1.0673171E-002   PE =  0.00712
The correlation coeff is  -0.40642

The min, mean, max are         0.09043,    0.11606,    0.13717
The standard deviation is  0.01152   rel. dev = 9.9 %

Cal = -0.00015 X (Julian Date - 150) +  0.12616
```



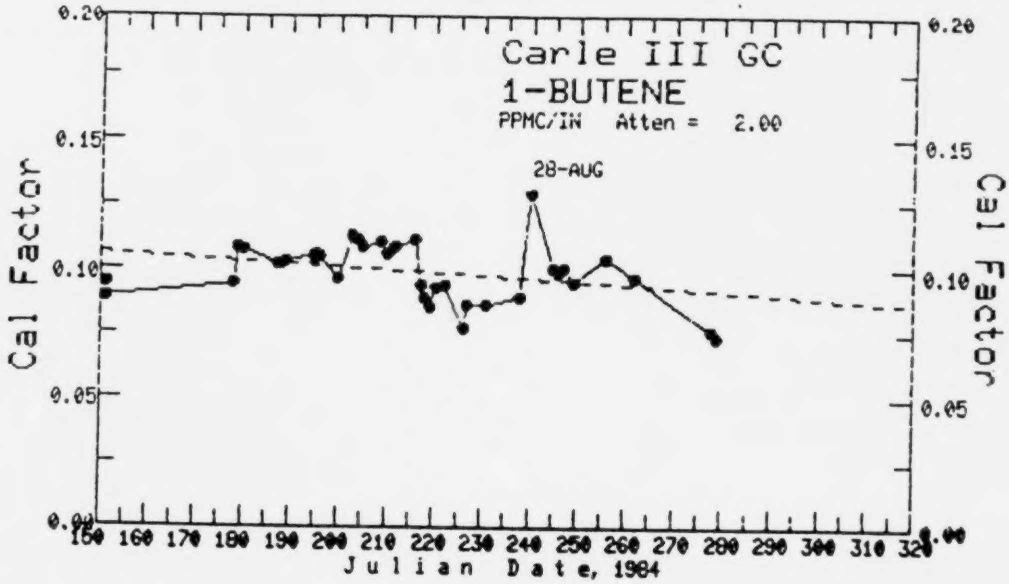
```
For the species TRANS-2-BUTENE and the instrument Carle III GC:

Beginning Caldate:             30-MAY-84
                         Day:  150
Ending     Caldate:            16-NOV-84
                         Day:  320
Upper CalFactor Limit             0.30000
Lower CalFactor Limit             0.00000

The number of data points       50
The number included  was        50
The slope of this fit  is -1.273805E-004
       with a std dev of 4.6032130E-005   rel. dev = -36.1 %
The intercept is          1.4263830E-001
       with a std dev of 1.0106748E-002   rel. dev = 7.1 %
The std dev of the fit is 9.9038982E-003   PE =  0.00660
The correlation coeff is  -0.37092

The min, mean, max are        0.09145,    0.11494,    0.13217
The standard deviation is  0.01056   rel. dev = 9.2 %

Cal = -0.00013 X (Julian Date - 150) +  0.12353

                     ...press RETURN-key when ready...
```



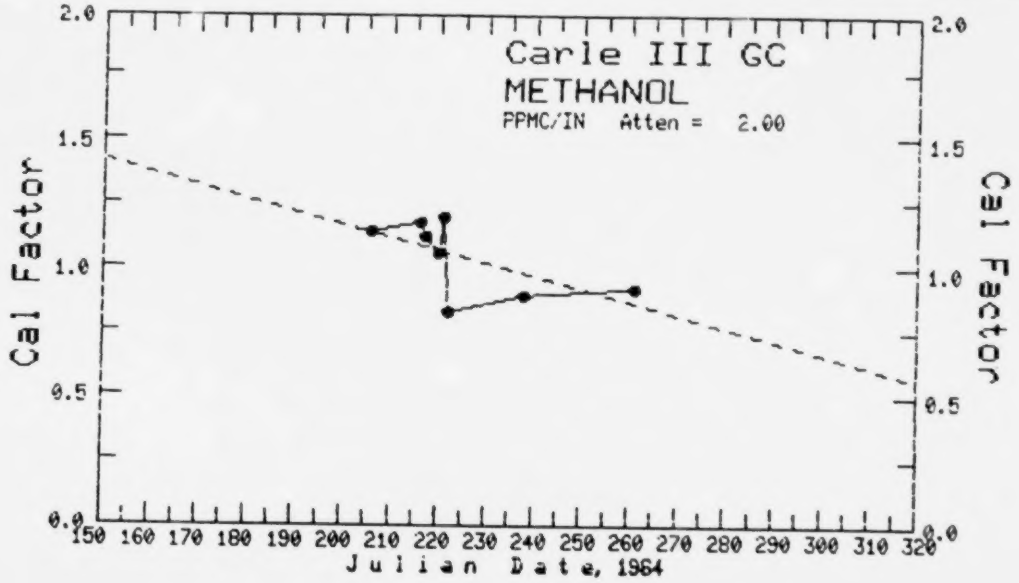
```
For the species ISOPENTANE and the instrument Carle III GC:

Beginning Caldate:          30-MAY-84
                    Day:    150
Ending    Caldate:          16-NOV-84
                    Day:    320
Upper CalFactor Limit           0.40000
Lower CalFactor Limit           0.00000

The number of data points       60
The number included  was        60
The slope of this fit  is -1.222656E-004
      with a std dev of 5.6003271E-005    rel. dev = -45.8 %
The intercept is          2.2209272E-001
      with a std dev of 1.2738738E-002    rel. dev = 5.7 %
The std dev of the fit is 1.6698649E-002  PE =  0.01113
The correlation coeff is  -0.27557

The min, mean, max are       0.15986,    0.19468,    0.23074
The standard deviation is  0.01722   rel. dev = 8.8 %

Cal = -0.00012 X (Julian Date - 150) +  0.20375

                    ...press RETURN-key when ready...
```



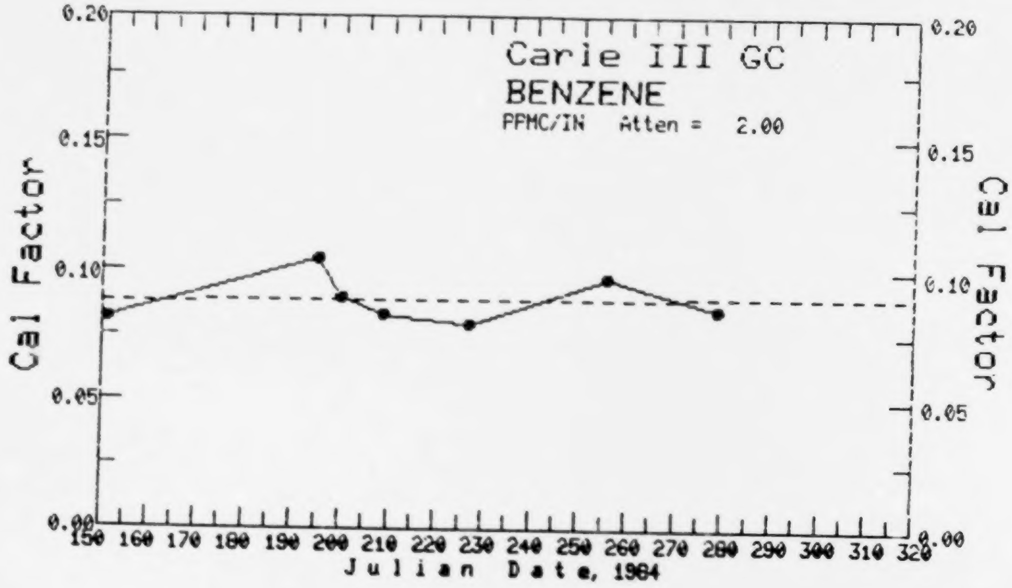
```
For the species N-PENTANE and the instrument Carle III GC:

Beginning Caldate:          30-MAY-84
                      Day:  150
Ending    Caldate:          16-NOV-84
                      Day:  320
Upper CalFactor Limit          0.60000
Lower CalFactor Limit          0.00000

The number of data points      45
The number included  was       45
The slope of this fit  is -2.873216E-004
        with a std dev of 1.0329445E-004   rel. dev = -36.0 %
The intercept is          3.5367520E-001
        with a std dev of 2.3728269E-002   rel. dev = 6.7 %
The std dev of the fit is 2.6308086E-002   PE =  0.01754
The correlation coeff is  -0.39051

The min, mean, max are       0.22760,    0.28858,    0.34680
The standard deviation is  0.02825   rel. dev = 9.8 %

Cal = -0.00029 X (Julian Date - 150) +  0.31058

                      ...press RETURN-key when ready...
```



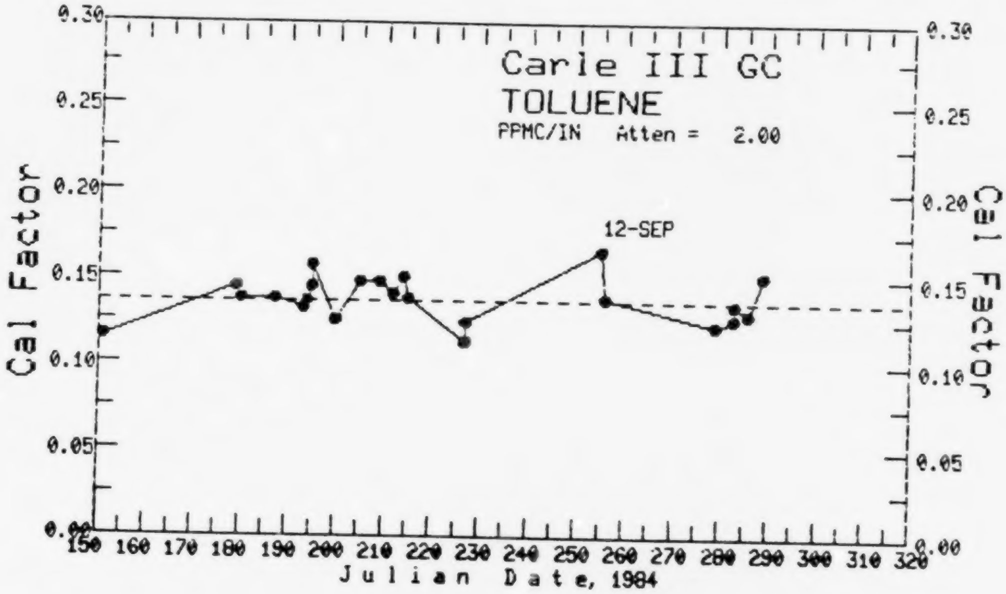
```
For the species 1-BUTENE and the instrument Carle III GC:

Beginning Caldate:            30-MAY-84
                      Day:    150
Ending     Caldate:           16-NOV-84
                      Day:    320
Upper CalFactor Limit            0.20000
Lower CalFactor Limit            0.00000

The number of data points        38
The number included  was         38
The slope of this fit  is -1.182031E-004
        with a std dev of 5.9781057E-005   rel. dev = -50.6 %
The intercept is          1.2497382E-001
        with a std dev of 1.2990315E-002   rel. dev = 10.4 %
The std dev of the fit is 1.1003754E-002   PE =  0.00734
The correlation coeff is  -0.31299

The min, mean, max are        0.07366,     0.09953,     0.12998
The standard deviation is  0.01143    rel. dev = 11.5 %

Cal = -0.00012 X (Julian Date - 150) +  0.10724

                       ...press RETURN-key when ready...
```



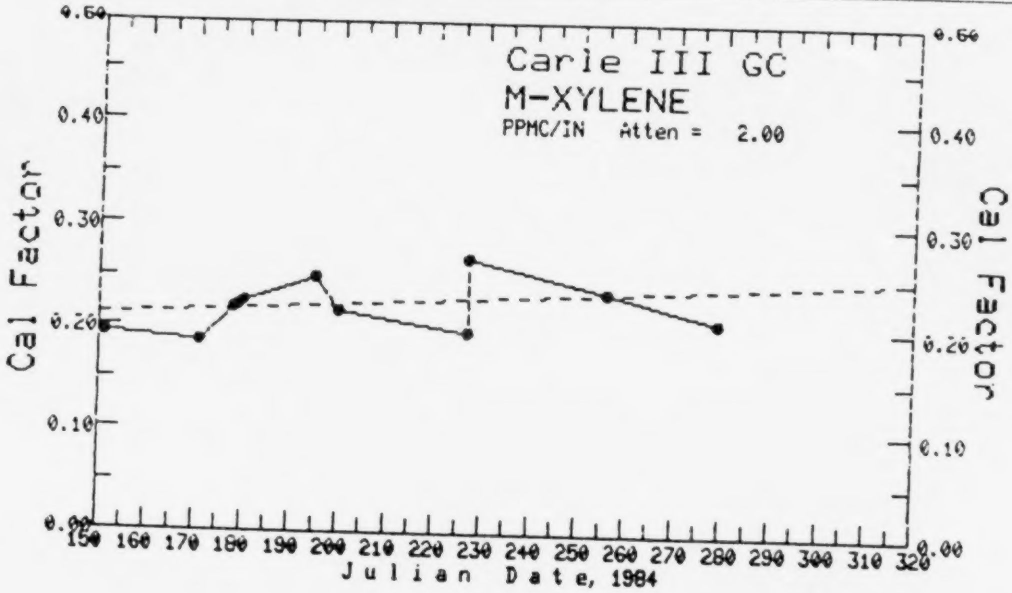
```
For the species METHANOL and the instrument Carle III GC:

Beginning Caldate:             30-MAY-84
                    Day:       150
Ending    Caldate:             16-NOV-84
                    Day:       320
Upper CalFactor Limit             2.00000
Lower CalFactor Limit             0.00000

The number of data points         8
The number included  was          8
The slope of this fit  is -5.071507E-003
      with a std dev of 2.7547702E-003   rel. dev = -54.3 %
The intercept is          2.1918042E+000
      with a std dev of 6.2171127E-001   rel. dev = 28.4 %
The std dev of the fit is 1.2383833E-001   PE =  0.08256
The correlation coeff is  -0.60081

The min, mean, max are        0.83510,    1.05008,    1.20625
The standard deviation is  0.14342   rel. dev = 13.7 %

Cal = -0.00507 X (Julian Date - 150) +  1.43108

                         ...press RETURN-key when ready...
```



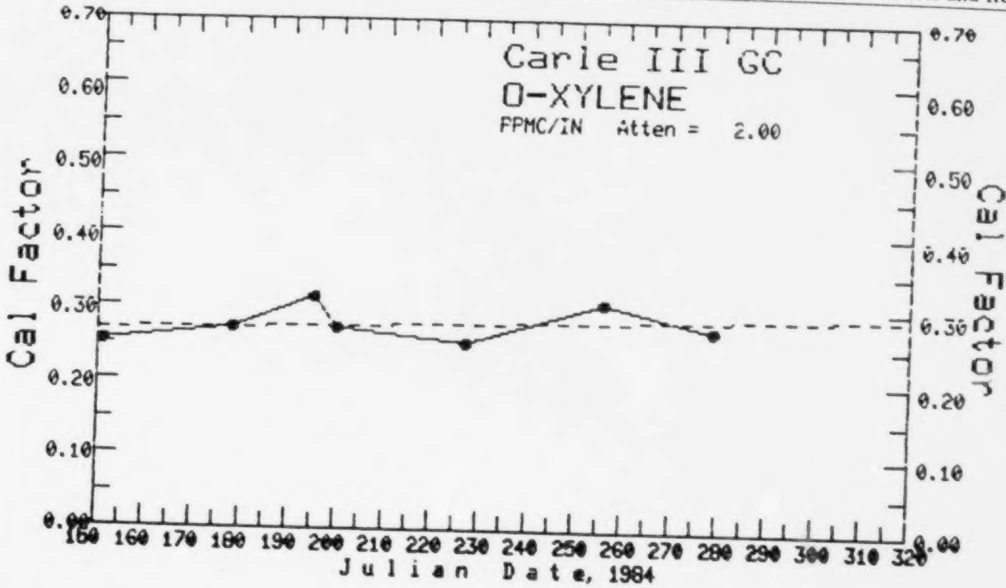
```
For the species BENZENE and the instrument Carle III GC:

Beginning Caldate:            30-MAY-84
                        Day:  150
Ending     Caldate:           16-NOV-84
                        Day:  320
Upper CalFactor Limit            0.20000
Lower CalFactor Limit            0.00000

The number of data points         7
The number included  was          7
The slope of this fit  is 1.0564688E-005
        with a std dev of 9.7659602E-005   rel. dev = 924.4 %
The intercept is          8.7323874E-002
        with a std dev of 2.1504541E-002   rel. dev = 24.6 %
The std dev of the fit is 1.0081872E-002   PE =  0.00672
The correlation coeff is    0.04832

The min, mean, max are        0.08022,    0.08961,    0.10564
The standard deviation is  0.00921   rel. dev = 10.3 %

Cal =  0.00001 X (Julian Date - 150) +  0.08891

                        ...press RETURN-key when ready...
```



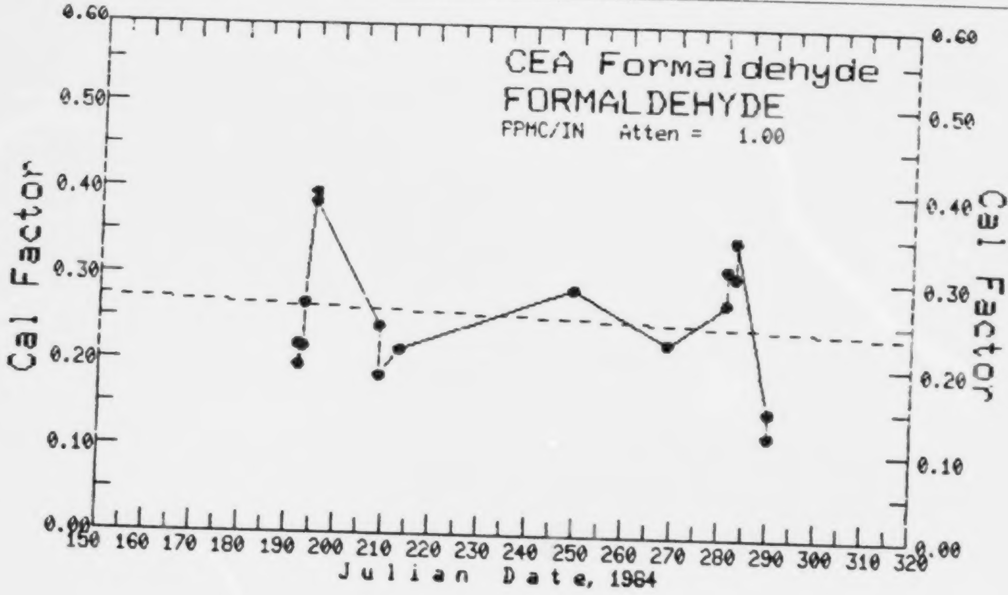
```
For the species TOLUENE and the instrument Carle III GC:

Beginning Caldate:           30-MAY-84
                      Day:   150
Ending     Caldate:          16-NOV-84
                      Day:   320
Upper CalFactor Limit          0.30000
Lower CalFactor Limit          0.00000

The number of data points      25
The number included  was       25
The slope of this fit  is 9.4526308E-007
        with a std dev of 7.3484704E-005   rel. dev = 7774.0 %
The intercept is          1.3672349E-001
        with a std dev of 1.6525408E-002   rel. dev = 12.1 %
The std dev of the fit is 1.3980213E-002   PE =  0.00932
The correlation coeff is   0.00268

The min, mean, max are         0.11350,    0.13693,    0.16721
The standard deviation is  0.01369   rel. dev = 10.0 %

Cal =  0.00000 X (Julian Date - 150) +  0.13687

                    ...press RETURN-key when ready...
```



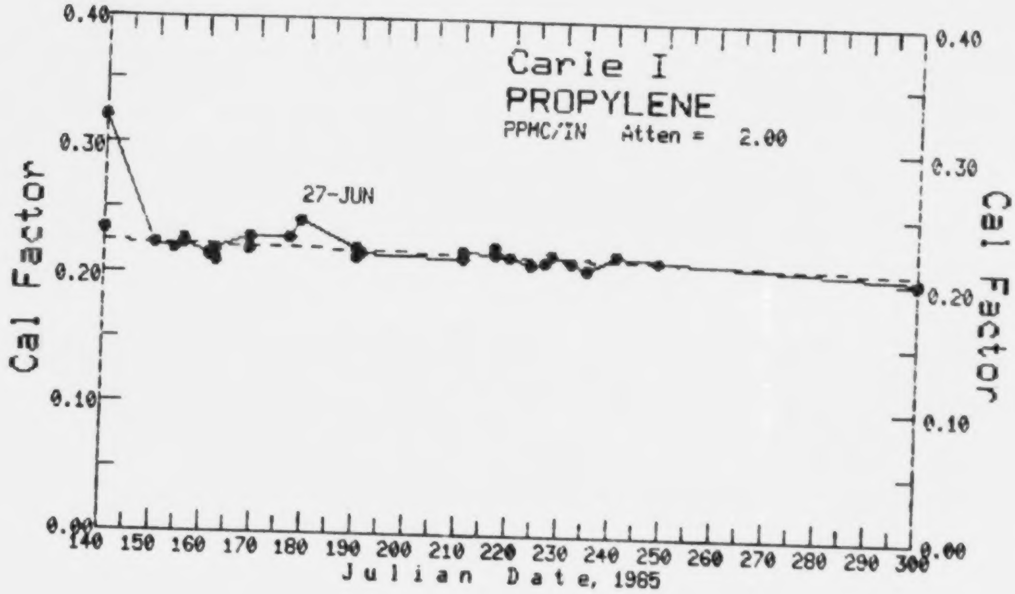
```
For the species M-XYLENE and the instrument Carle III GC:

Beginning Caldate:            30-MAY-84
                    Day:      150
Ending     Caldate:           16-NOV-84
                    Day:      320
Upper CalFactor Limit            0.50000
Lower CalFactor Limit            0.00000

The number of data points      12
The number included  was       12
The slope of this fit  is 2.2924388E-004
        with a std dev of 2.1399147E-004    rel. dev = 93.3 %
The intercept is          1.7734365E-001
        with a std dev of 4.4723535E-002    rel. dev = 25.2 %
The std dev of the fit is 2.6853727E-002    PE =  0.01790
The correlation coeff is    0.32086

The min, mean, max are        0.18690,     0.22453,     0.26853
The standard deviation is  0.02703   rel. dev = 12.0 %

Cal =  0.00023 X (Julian Date - 150) +  0.21173

                     ...press RETURN-key when ready...
```



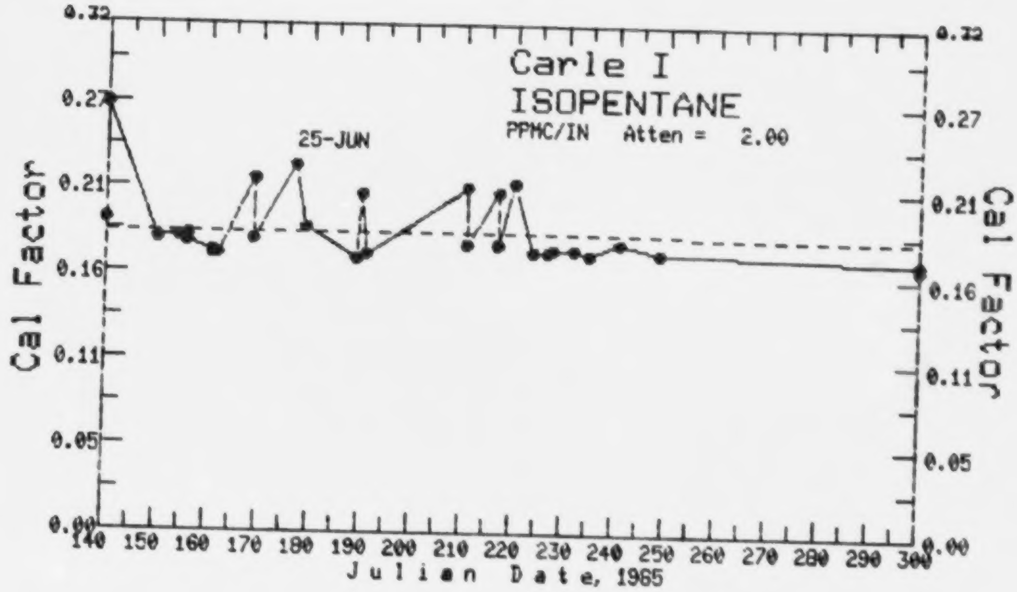
```
For the species O-XYLENE and the instrument Carle III GC:

Beginning Caldate:             30-MAY-84
                         Day:  150
Ending    Caldate:             16-NOV-84
                         Day:  320
Upper CalFactor Limit            0.70000
Lower CalFactor Limit            0.00000

The number of data points        7
The number included  was         7
The slope of this fit  is 1.3699588E-004
      with a std dev of 2.3682240E-004   rel. dev = 172.9 %
The intercept is          2.5194653E-001
      with a std dev of 5.1218128E-002   rel. dev = 20.3 %
The std dev of the fit is 2.5898701E-002   PE =  0.01727
The correlation coeff is   0.25046

The min, mean, max are        0.25603,    0.28103,    0.31762
The standard deviation is  0.02442   rel. dev = 8.7 %

Cal =  0.00014 X (Julian Date - 150) +  0.27250
```



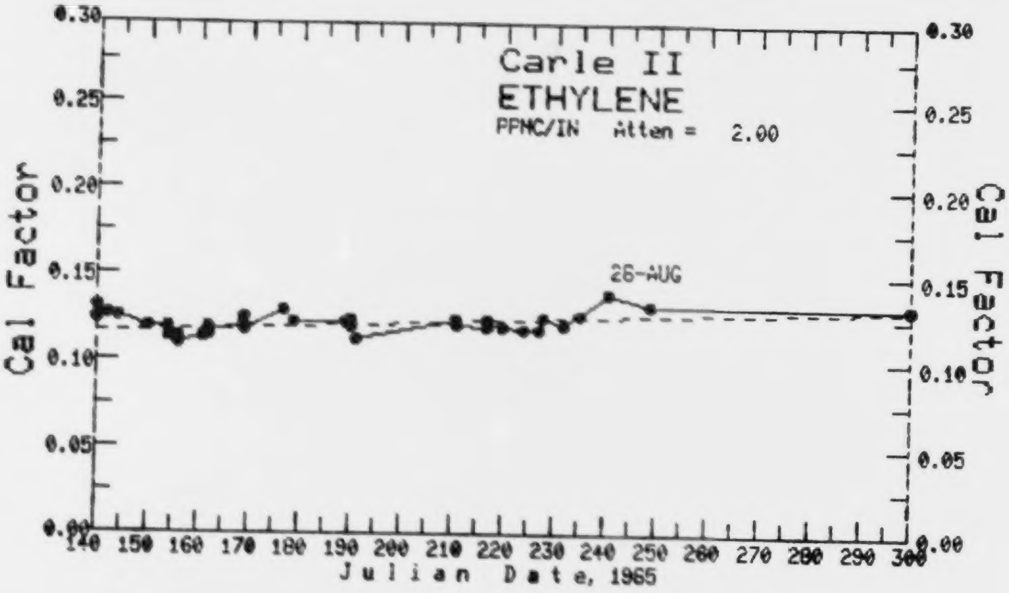
```
For the species FORMALDEHYDE and the instrument CEA Formaldehyde:

Beginning Caldate:              30-MAY-84
                         Day:   150
Ending    Caldate:              16-NOV-84
                         Day:   320
Upper CalFactor Limit              0.60000
Lower CalFactor Limit              0.00000

The number of data points          17
The number included  was           17
The slope of this fit  is -2.282711E-004
       with a std dev of 4.7236958E-004   rel. dev = -206.9 %
The intercept is          3.1092736E-001
       with a std dev of 1.1328004E-001   rel. dev = 36.4 %
The std dev of the fit is 7.9710921E-002   PE =  0.05314
The correlation coeff is  -0.12381

The min, mean, max are        0.12160,    0.25699,    0.39930
The standard deviation is  0.07778   rel. dev = 30.3 %

Cal = -0.00023 X (Julian Date - 150) +  0.27669

                   ...press RETURN-key when ready...
```



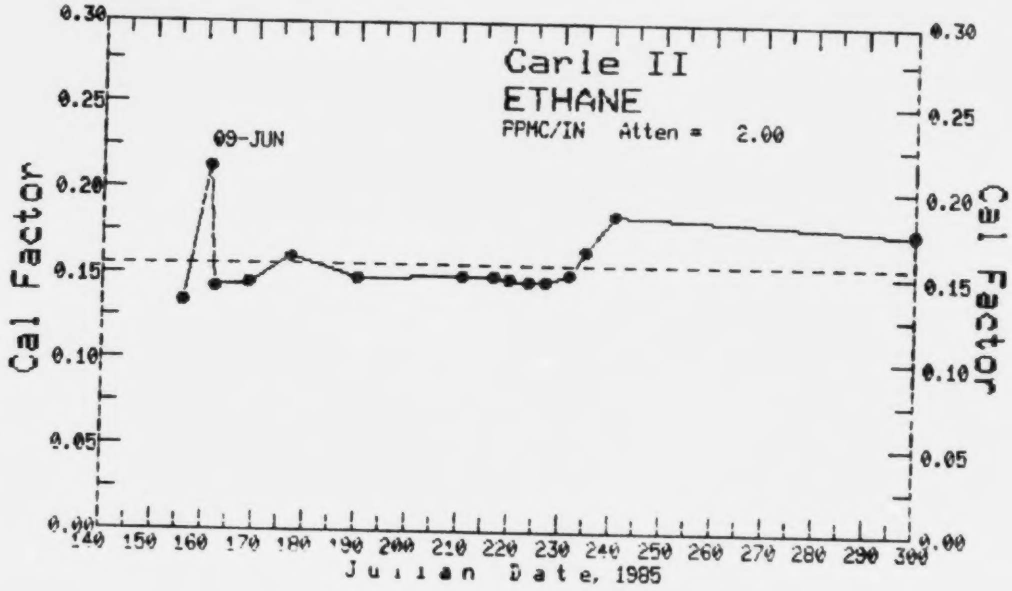
```
For the species PROPYLENE and the instrument Carle I:

Beginning Caldate:             19-MAY-85
                         Day:  140
Ending    Caldate:             26-OCT-85
                         Day:  300
Upper CalFactor Limit              0.40000
Lower CalFactor Limit              0.00000

The number of data points          33
The number included  was           29
The slope of this fit  is   -1.031921E-004
       with a std dev of    3.9748294E-005     rel. dev = -38.5 %
The intercept is            2.3982757E-001
       with a std dev of    7.7330116E-003     rel. dev = 3.2 %
The std dev of the fit is   6.6287787E-003     PE =   0.00442
The correlation coeff is    -0.44695

The min, mean, max are          0.20126,     0.22001,     0.32267
The standard deviation is    0.00728    rel. dev = 3.3 %

Cal = -0.00010 X (Julian Date - 140) +  0.22538
```



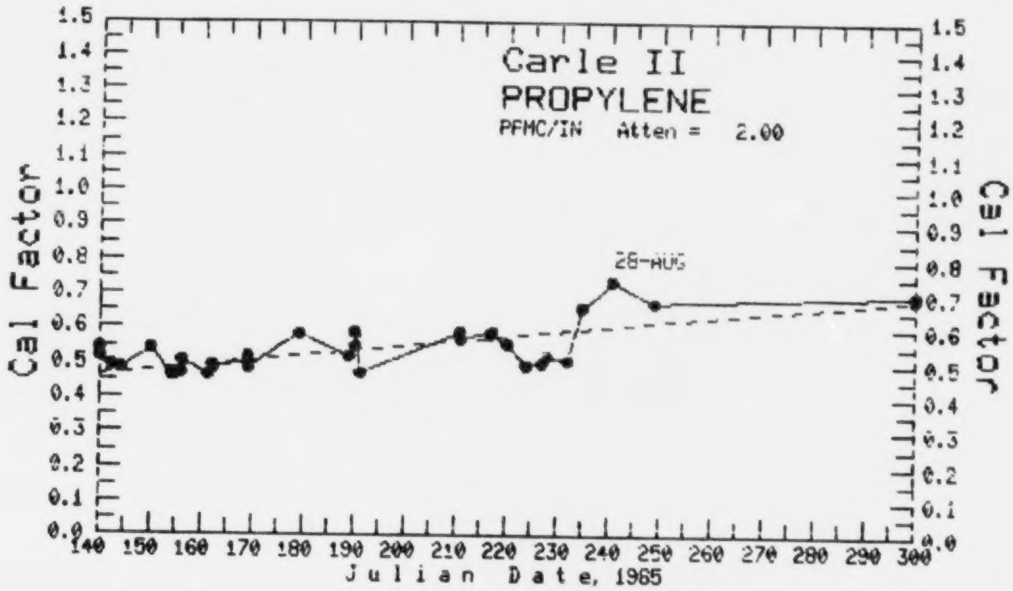
```
For the species ISOPENTANE and the instrument Carle I:

Beginning Caldate:          19-MAY-85
                     Day:   140
Ending    Caldate:          26-OCT-85
                     Day:   300
Upper CalFactor Limit          0.32000
Lower CalFactor Limit          0.00000

The number of data points      31
The number included  was       27
The slope of this fit  is -1.768853E-005
        with a std dev of 1.1176868E-004    rel. dev = -631.9 %
The intercept is          1.9003641E-001
        with a std dev of 2.1961717E-002    rel. dev = 11.6 %
The std dev of the fit is 1.8118941E-002    PE =  0.01208
The correlation coeff is  -0.03164

The min, mean, max are        0.16862,     0.18660,     0.26693
The standard deviation is  0.01778    rel. dev = 9.5 %

Cal = -0.00002 X (Julian Date - 140) +  0.18756
```



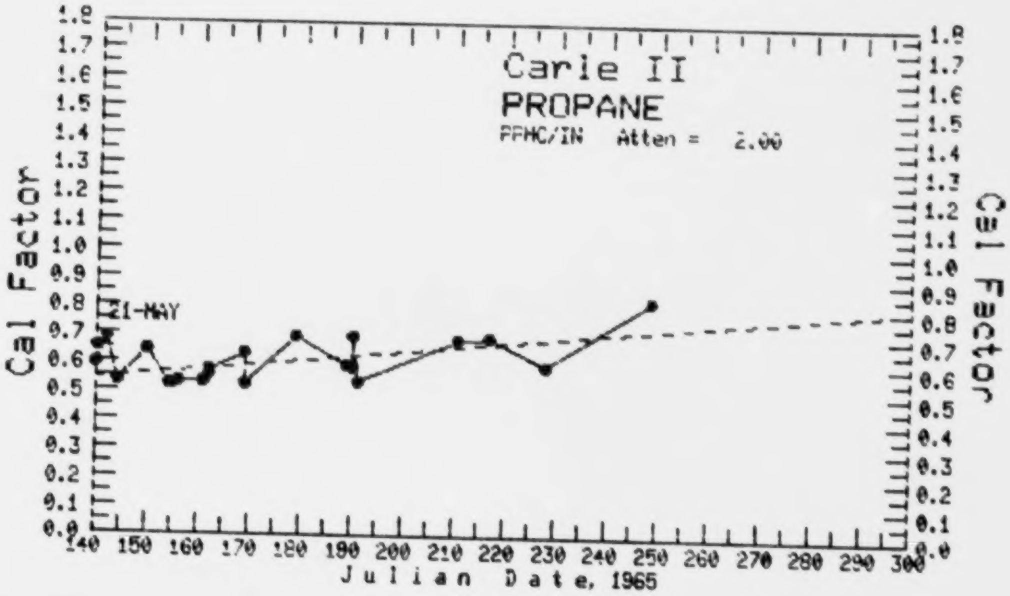
```
For the species ETHYLENE and the instrument Carle II:

Beginning Caldate:           19-MAY-85
                       Day:  140
Ending    Caldate:           26-OCT-85
                       Day:  300
Upper CalFactor Limit           0.30000
Lower CalFactor Limit           0.00000

The number of data points       39
The number included  was        35
The slope of this fit  is 9.1951491E-005
        with a std dev of 2.8164536E-005   rel. dev = 30.6 %
The intercept is          1.0481323E-001
        with a std dev of 5.3398102E-003   rel. dev = 5.1 %
The std dev of the fit is 5.2356481E-003   PE =  0.00349
The correlation coeff is   0.49411

The min, mean, max are       0.11123,    0.12201,    0.14018
The standard deviation is  0.00593   rel. dev = 4.9 %

Cal =  0.00009 X (Julian Date - 140) +  0.11769
```



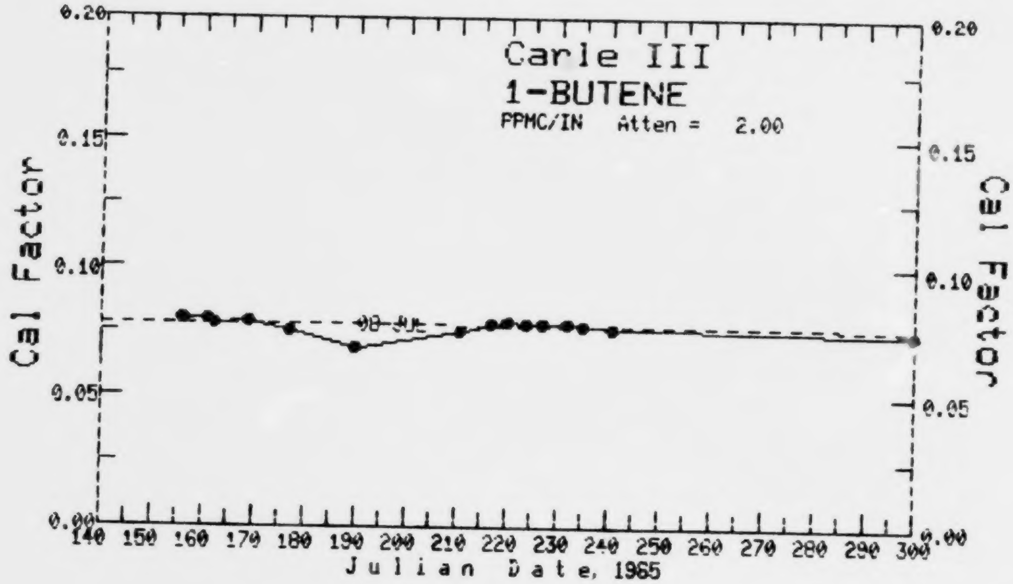
```
For the species ETHANE and the instrument Carle II:

Beginning Caldate:          19-MAY-85
                      Day:  140
Ending    Caldate:          26-OCT-85
                      Day:  300
Upper CalFactor Limit          0.30000
Lower CalFactor Limit          0.00000

The number of data points      16
The number included  was       14
The slope of this fit  is 2.5593750E-006
       with a std dev of 1.9228907E-004    rel. dev = 7513.1 %
The intercept is          1.5613441E-001
       with a std dev of 3.9183586E-002    rel. dev = 25.1 %
The std dev of the fit is 2.1499800E-002   PE =  0.01433
The correlation coeff is   0.00384

The min, mean, max are        0.13446,    0.15665,    0.21470
The standard deviation is  0.02066    rel. dev = 13.2 %

Cal =  0.00000 X (Julian Date - 140) +  0.15649
```



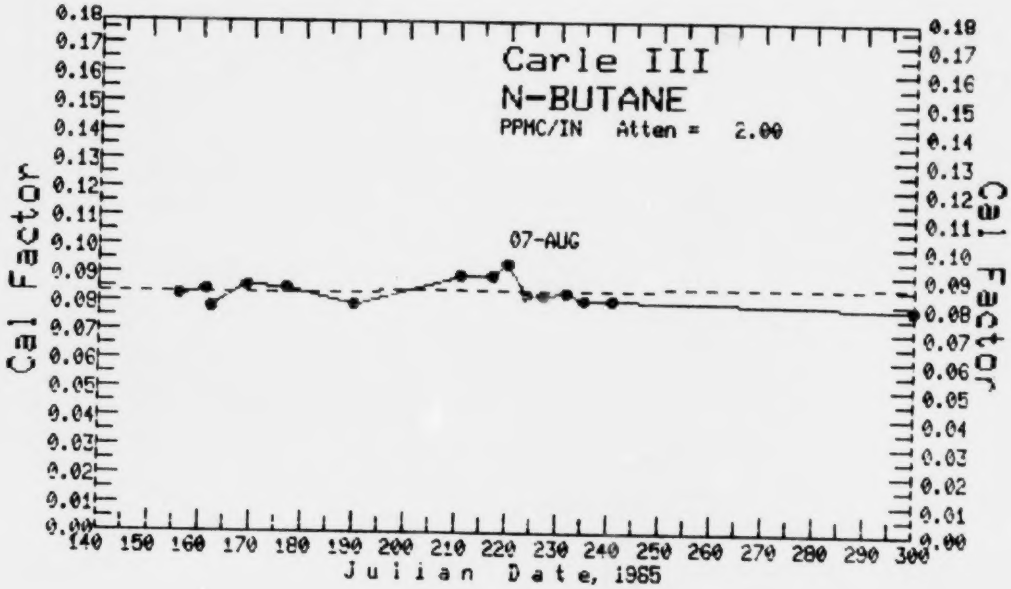
```
For the species PROPYLENE and the instrument Carle II:

Beginning Caldate:          19-MAY-85
                      Day:  140
Ending    Caldate:          26-OCT-85
                      Day:  300
Upper CalFactor Limit          1.50000
Lower CalFactor Limit          0.00000

The number of data points     37
The number included  was      33
The slope of this fit  is 1.3951261E-003
      with a std dev of 2.6665881E-004    rel. dev = 19.1 %
The intercept is          2.7021178E-001
      with a std dev of 5.0867805E-002    rel. dev = 18.8 %
The std dev of the fit is 4.8983910E-002    PE =  0.03266
The correlation coeff is   0.68478

The min, mean, max are        0.46068,     0.53258,     0.73353
The standard deviation is  0.06616   rel. dev = 12.4 %

Cal =  0.00140 X (Julian Date - 140) +  0.46553
```



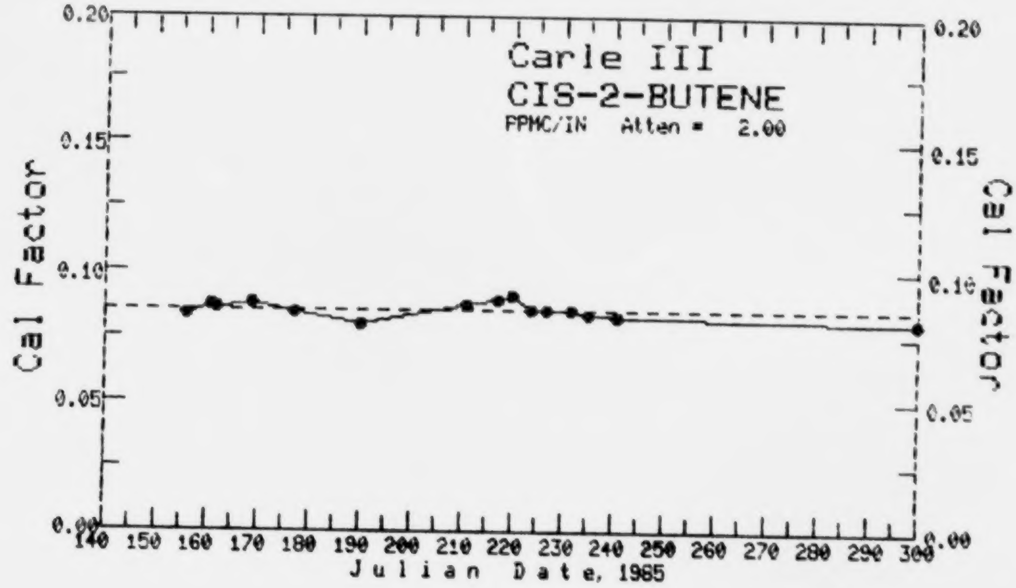
```
For the species PROPANE and the instrument Carle II:

Beginning Caldate:             19-MAY-85
                         Day:  140
Ending    Caldate:             26-OCT-85
                         Day:  300
Upper CalFactor Limit             1.80000
Lower CalFactor Limit             0.00000

The number of data points         22
The number included  was          20
The slope of this fit  is 1.6650439E-003
      with a std dev of 5.2358088E-004    rel. dev = 31.4 %
The intercept is          3.1646586E-001
      with a std dev of 9.4610790E-002    rel. dev = 29.9 %
The std dev of the fit is 6.7285338E-002    PE =   0.04486
The correlation coeff is   0.59977

The min, mean, max are         0.53173,    0.61351,    0.82884
The standard deviation is  0.08185    rel. dev = 13.3 %

Cal =  0.00167 X (Julian Date - 140) +  0.54957
```



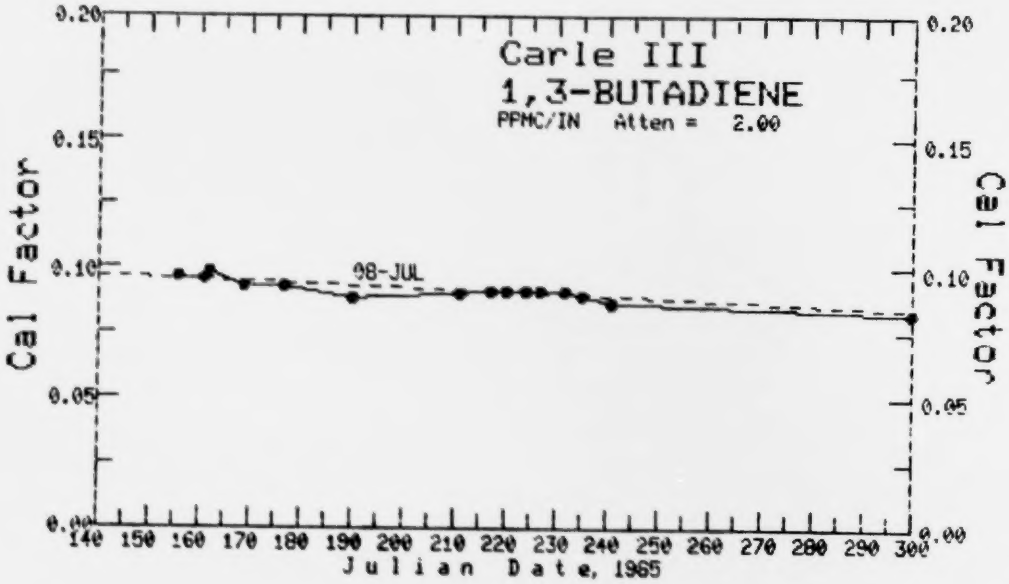
```
For the species 1-BUTENE and the instrument Carle III:

Beginning Caldate:          19-MAY-85
                      Day:  140
Ending    Caldate:          26-OCT-85
                      Day:  300
Upper CalFactor Limit          0.20000
Lower CalFactor Limit          0.00000

The number of data points      15
The number included  was       14
The slope of this fit  is  -8.967689E-006
       with a std dev of  2.6904638E-005   rel. dev = -300.0 %
The intercept is          7.9523590E-002
       with a std dev of  5.4824760E-003   rel. dev = 6.9 %
The std dev of the fit is 3.0082018E-003   PE =  0.00201
The correlation coeff is  -0.09578

The min, mean, max are        0.06901,    0.07772,    0.08054
The standard deviation is  0.00290   rel. dev = 3.7 %

Cal = -0.00001 X (Julian Date - 140) +  0.07827
```



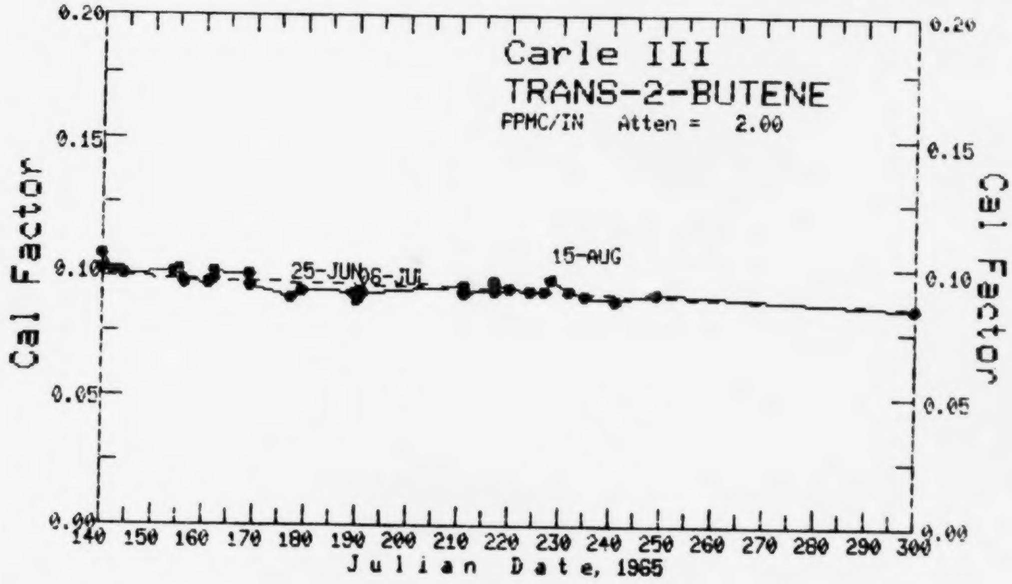
```
For the species N-BUTANE and the instrument Carle III:

Beginning Caldate:          19-MAY-85
                      Day:  140
Ending    Caldate:          26-OCT-85
                      Day:  300
Upper CalFactor Limit          0.18000
Lower CalFactor Limit          0.00000

The number of data points      15
The number included  was       14
The slope of this fit  is  1.5981758E-005
      with a std dev of  3.9174523E-005    rel. dev = 245.1 %
The intercept is           8.1616341E-002
      with a std dev of  7.9827643E-003    rel. dev = 9.8 %
The std dev of the fit is  4.3800951E-003    PE =  0.00292
The correlation coeff is    0.11696

The min, mean, max are         0.07902,     0.08484,     0.09427
The standard deviation is   0.00424    rel. dev = 5.0 %

Cal =  0.00002 X (Julian Date - 140) +  0.08385
```



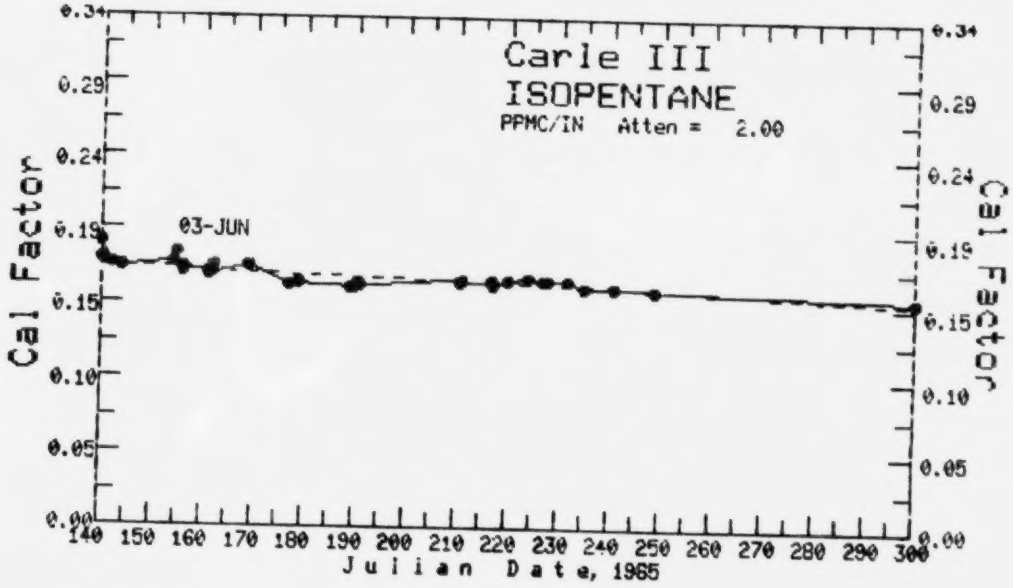
```
For the species CIS-2-BUTENE and the instrument Carle III:

Beginning Caldate:            19-MAY-85
                    Day:      140
Ending    Caldate:            26-OCT-85
                    Day:      300
Upper CalFactor Limit             0.20000
Lower CalFactor Limit             0.00000

The number of data points         15
The number included  was          14
The slope of this fit  is -8.087915E-007
      with a std dev of 2.4874599E-005    rel. dev = -3075.5 %
The intercept is          8.6455719E-002
      with a std dev of 5.0688061E-003    rel. dev = 5.9 %
The std dev of the fit is 2.7812236E-003  PE =  0.00185
The correlation coeff is  -0.00939

The min, mean, max are        0.08079,     0.08629,     0.09119
The standard deviation is  0.00267   rel. dev = 3.1 %

Cal = -0.00000 X (Julian Date - 140) +  0.08634
```



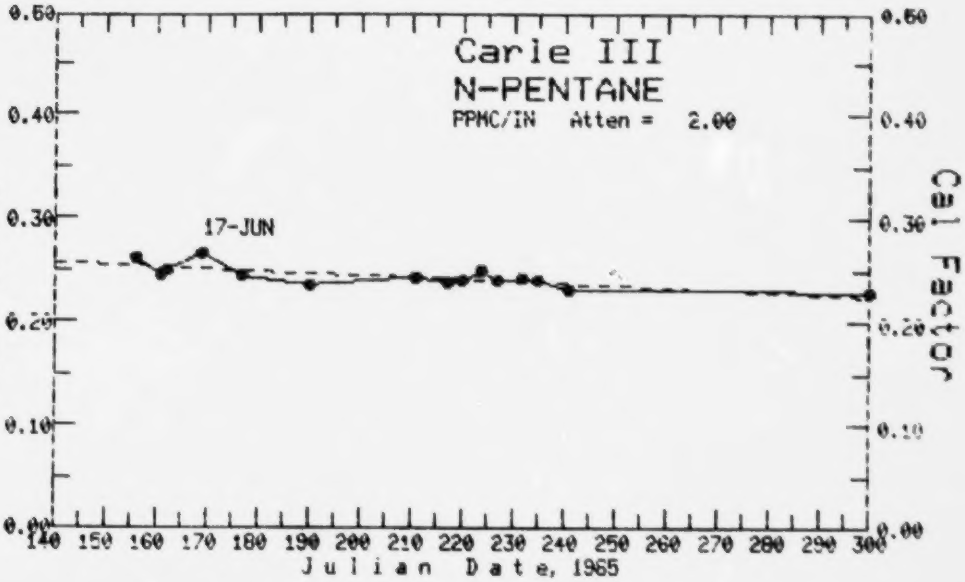
```
For the species 1,3-BUTADIENE and the instrument Carle III:

Beginning Caldate:          19-MAY-85
                     Day:   140
Ending    Caldate:          26-OCT-85
                     Day:   300
Upper CalFactor Limit          0.20000
Lower CalFactor Limit          0.00000

The number of data points      15
The number included  was       14
The slope of this fit  is  -7.957409E-005
      with a std dev of   1.7358994E-005    rel. dev = -21.8 %
The intercept is           1.0849807E-001
      with a std dev of   3.5373184E-003    rel. dev = 3.3 %
The std dev of the fit is 1.9409055E-003    PE =  0.00129
The correlation coeff is  -0.79782

The min, mean, max are         0.08310,     0.09246,     0.09884
The standard deviation is  0.00309    rel. dev = 3.3 %

Cal = -0.00008 X (Julian Date - 140) +  0.09736
```



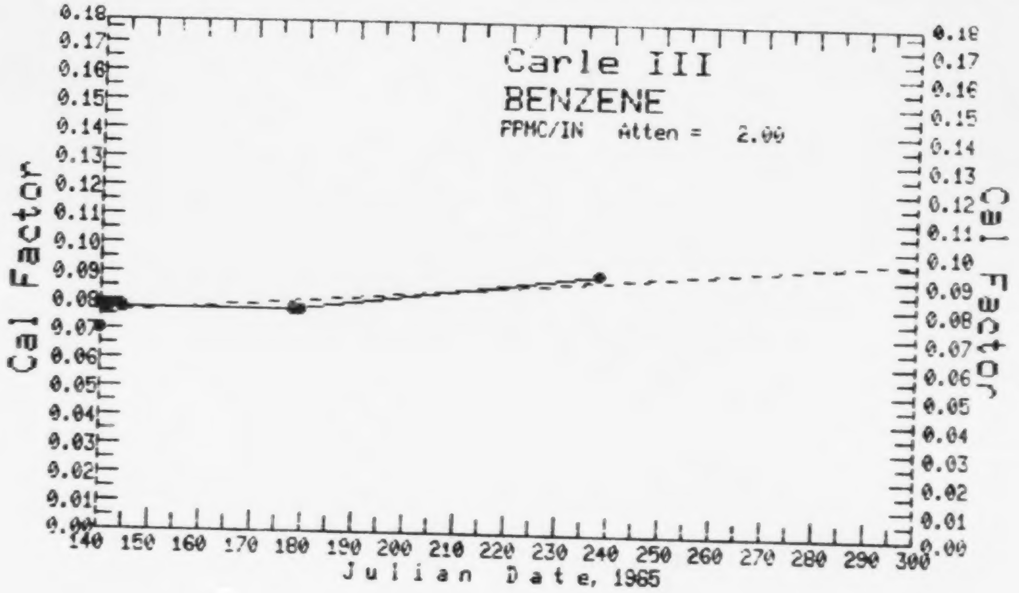
```
For the species TRANS-2-BUTENE and the instrument Carle III:

Beginning Caldate:             19-MAY-85
                        Day:   140
Ending     Caldate:            26-OCT-85
                        Day:   300
Upper CalFactor Limit             0.20000
Lower CalFactor Limit             0.00000

The number of data points         33
The number included  was          30
The slope of this fit  is  -7.210258E-005
       with a std dev of  1.5605839E-005    rel. dev = -21.6 %
The intercept is          1.0738269E-001
       with a std dev of  3.0166494E-003    rel. dev = 2.8 %
The std dev of the fit is 2.7363656E-003    PE =  0.00182
The correlation coeff is  -0.65771

The min, mean, max are        0.08489,     0.09364,     0.10539
The standard deviation is  0.00357    rel. dev = 3.8 %

Cal = -0.00007 X (Julian Date - 140) +  0.09729
```



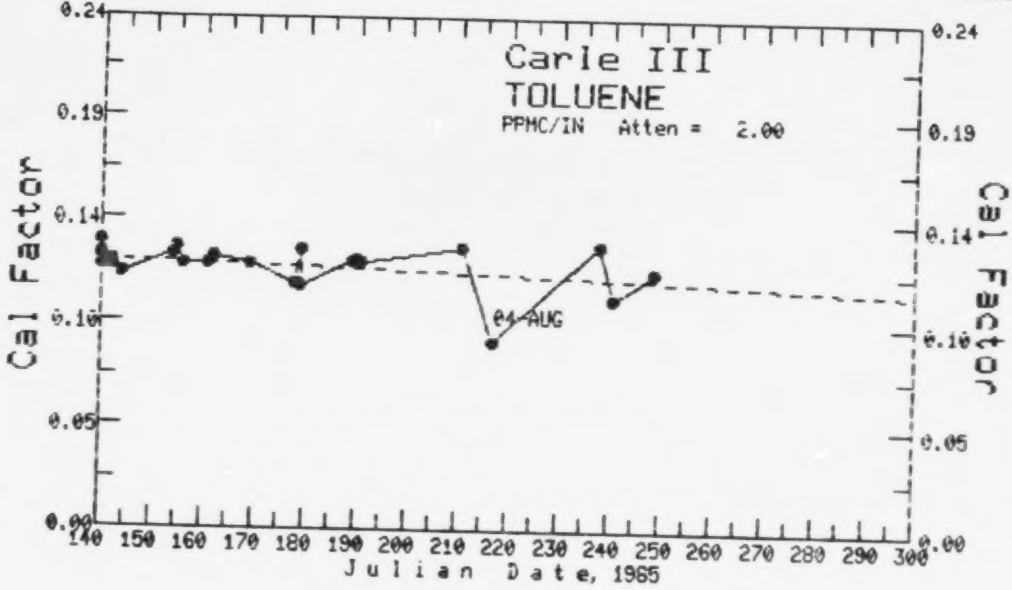
```
For the species ISOPENTANE and the instrument Carle III:

Beginning Caldate:              19-MAY-85
                         Day:   140
Ending    Caldate:              26-OCT-85
                         Day:   300
Upper CalFactor Limit              0.34000
Lower CalFactor Limit              0.00000

The number of data points          33
The number included  was           30
The slope of this fit  is  -1.351515E-004
       with a std dev of   2.4010991E-005    rel. dev = -17.8 %
The intercept is           1.9142729E-001
       with a std dev of   4.6413872E-003    rel. dev = 2.4 %
The std dev of the fit is  4.2101454E-003    PE =  0.00281
The correlation coeff is   -0.72860

The min, mean, max are         0.15300,    0.16566,    0.18676
The standard deviation is  0.00604    rel. dev = 3.6 %

Cal = -0.00014 X (Julian Date - 140) +  0.17251
```



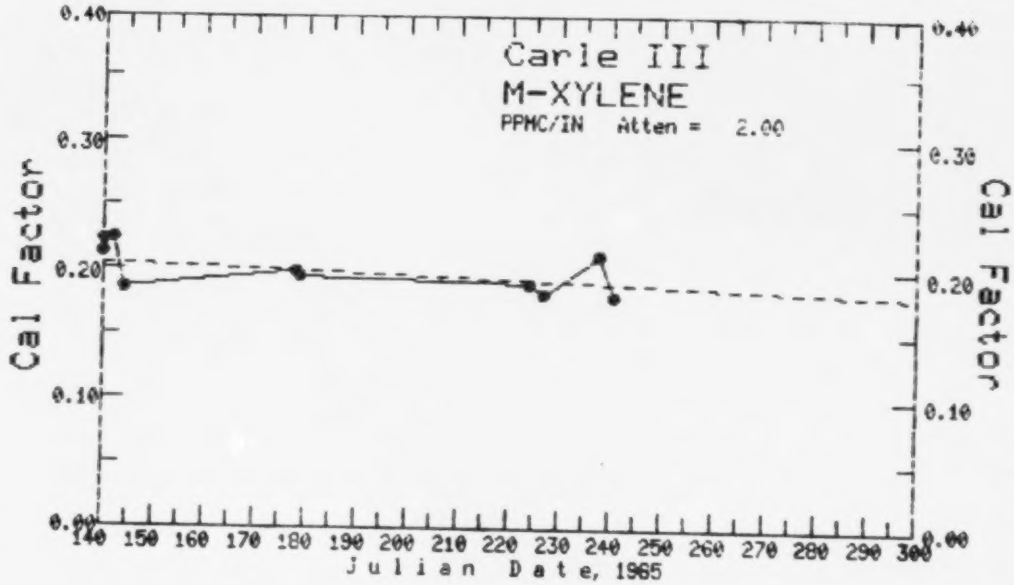
```
For the species N-PENTANE and the instrument Carle III:

Beginning Caldate:          19-MAY-85
                     Day:   140
Ending    Caldate:          26-OCT-85
                     Day:   300
Upper CalFactor Limit          0.50000
Lower CalFactor Limit          0.00000

The number of data points      15
The number included  was       14
The slope of this fit  is -2.057068E-004
       with a std dev of 6.6781722E-005   rel. dev = -32.5 %
The intercept is          2.8669104E-001
       with a std dev of 1.3608404E-002   rel. dev = 4.7 %
The std dev of the fit is 7.4668501E-003   PE =  0.00498
The correlation coeff is  -0.66449

The min, mean, max are        0.22943,     0.24523,     0.26701
The standard deviation is  0.00960   rel. dev = 3.9 %

Cal = -0.00021 X (Julian Date - 140) +  0.25789
```



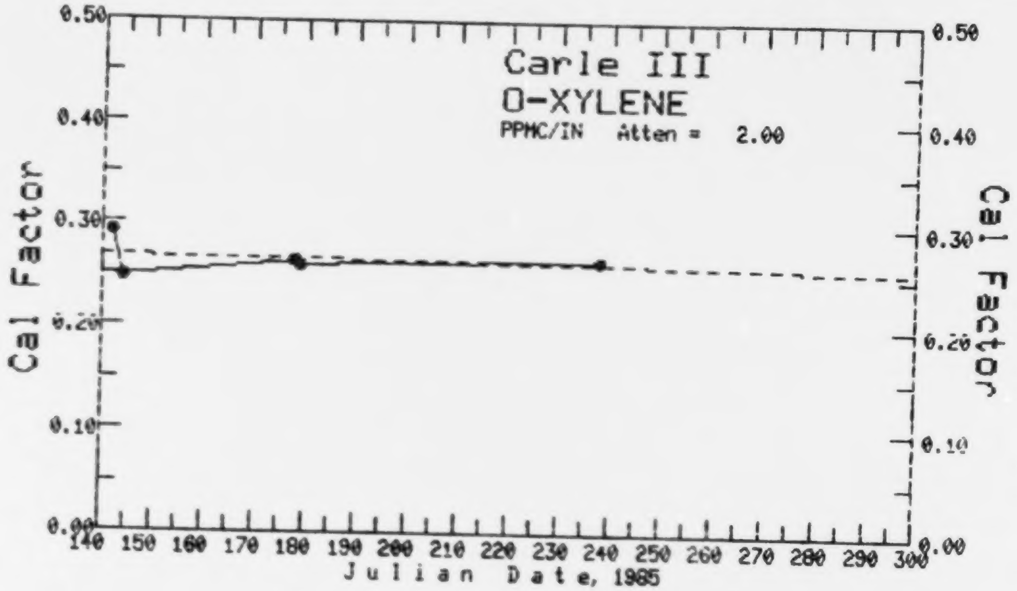
```
For the species BENZENE and the instrument Carle III:

Beginning Caldate:             19-MAY-85
                         Day:  140
Ending    Caldate:             26-OCT-85
                         Day:  300
Upper CalFactor Limit             0.18000
Lower CalFactor Limit             0.00000

The number of data points         7
The number included  was          5
The slope of this fit  is 1.3085192E-004
        with a std dev of 4.0742249E-005   rel. dev = 31.1 %
The intercept is          5.8023267E-002
        with a std dev of 7.3170403E-003   rel. dev = 12.6 %
The std dev of the fit is 3.1655443E-003   PE =  0.00211
The correlation coeff is   0.88017

The min, mean, max are        0.07062,     0.08108,     0.09140
The standard deviation is  0.00578   rel. dev = 7.1 %

Cal =  0.00013 X (Julian Date - 140) +  0.07634
```



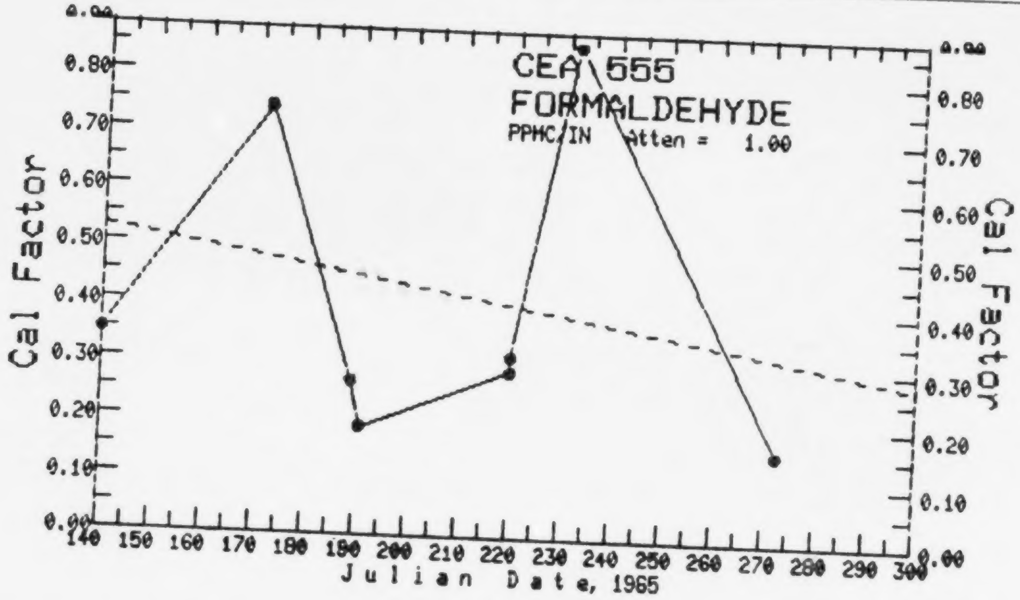
```
For the species TOLUENE and the instrument Carle III:

Beginning Caldate:           19-MAY-85
                       Day:  140
Ending    Caldate:           26-OCT-85
                       Day:  300
Upper CalFactor Limit          0.24000
Lower CalFactor Limit          0.00000

The number of data points      24
The number included  was       20
The slope of this fit  is -8.936442E-005
      with a std dev of 6.8168276E-005   rel. dev = -76.3 %
The intercept is          1.3793482E-001
      with a std dev of 1.2627435E-002   rel. dev = 9.2 %
The std dev of the fit is 9.9349386E-003  PE =  0.00662
The correlation coeff is  -0.29522

The min, mean, max are       0.08803,    0.12164,    0.13325
The standard deviation is  0.01012   rel. dev = 8.3 %

Cal = -0.00009 X (Julian Date - 140) +  0.12542
```



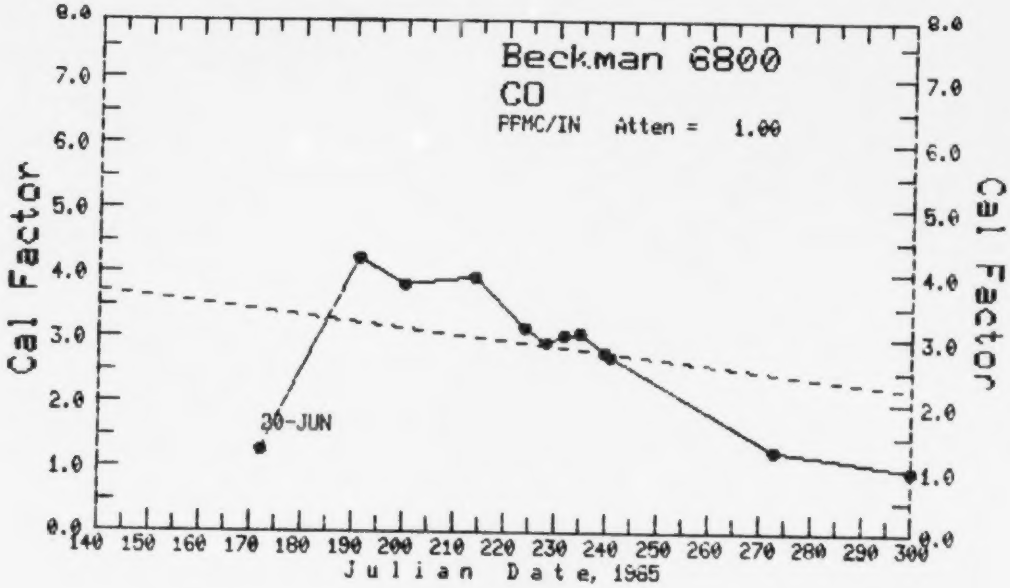
```
For the species M-XYLENE and the instrument Carle III:

Beginning Caldate:          19-MAY-85
                      Day:  140
Ending    Caldate:          26-OCT-85
                      Day:  300
Upper CalFactor Limit          0.40000
Lower CalFactor Limit          0.00000

The number of data points      10
The number included  was        8
The slope of this fit  is -1.503471E-004
        with a std dev of 1.4206482E-004    rel. dev = -94.5 %
The intercept is          2.2668426E-001
        with a std dev of 2.8459762E-002    rel. dev = 12.6 %
The std dev of the fit is 1.5408549E-002    PE =  0.01027
The correlation coeff is  -0.39661

The min, mean, max are        0.18045,    0.19712,    0.22562
The standard deviation is  0.01554   rel. dev = 7.9 %

Cal = -0.00015 X (Julian Date - 140) +  0.20564
```



```
For the species O-XYLENE and the instrument Carle III:

Beginning Caldate:          19-MAY-85
                    Day:    140
Ending    Caldate:          26-OCT-85
                    Day:    300
Upper CalFactor Limit          0.50000
Lower CalFactor Limit          0.00000

The number of data points      5
The number included  was       5
The slope of this fit  is  -7.718431E-005
        with a std dev of  2.3306011E-004     rel. dev = -302.0 %
The intercept is           2.7907738E-001
        with a std dev of  4.1856065E-002     rel. dev = 15.0 %
The std dev of the fit is  1.8108036E-002     PE =  0.01207
The correlation coeff is   -0.18780

The min, mean, max are        0.24868,    0.26548,    0.29183
The standard deviation is  0.01597   rel. dev = 6.0 %

Cal = -0.00008 X (Julian Date - 140) +  0.26827
```



```
For the species FORMALDEHYDE and the instrument CEA 555:

Beginning Caldate:            19-MAY-85
                        Day:  140
Ending    Caldate:            26-OCT-85
                        Day:  300
Upper CalFactor Limit            0.90000
Lower CalFactor Limit            0.00000

The number of data points         9
The number included  was          9
The slope of this fit  is -1.594734E-003
      with a std dev of  2.5116956E-003   rel. dev = -157.5 %
The intercept is          7.5697485E-001
      with a std dev of  5.1346482E-001   rel. dev = 67.8 %
The std dev of the fit is 2.8097332E-001   PE =  0.18732
The correlation coeff is  -0.23335

The min, mean, max are        0.15590,    0.43643,    0.86620
The standard deviation is  0.27029   rel. dev = 61.9 %

Cal = -0.00159 X (Julian Date - 140) +  0.53371
```



```
For the species CO and the instrument Beckman 6800:

Beginning Caldate:          19-MAY-85
                      Day:  140
Ending    Caldate:          26-OCT-85
                      Day:  300
Upper CalFactor Limit          8.00000
Lower CalFactor Limit          0.00000

The number of data points      12
The number included  was       11
The slope of this fit  is -9.602645E-003
        with a std dev of 1.1196663E-002   rel. dev = -116.6 %
The intercept is          5.0961892E+000
        with a std dev of 2.5111042E+000   rel. dev = 49.3 %
The std dev of the fit is 9.7598565E-001   PE =  0.65066
The correlation coeff is  -0.27487

The min, mean, max are        0.99360,     2.95742,     4.26480
The standard deviation is  0.96299   rel. dev = 32.6 %

Cal = -0.00960 X (Julian Date - 140) +  3.75182
```

E

# Solar/UV Radiation

The purpose of this section is to provide supporting information for the radiometry measurements taken at the UNC outdoor smog chamber during experiments conducted between 1973 and 1986.

## General Description Of Light Radiometers

Two types of light radiometers are used for measurement of light during the UNC smog chamber experiments. Both are manufactured by the Eppley Laboratory, Inc.

The Eppley Black and White Pyranometer, Model 8-48 measures total solar radiation (TSR). It is linear within plus or minus 1 percent with a response time of 5 seconds. The first pyranometer was purchased in 1972 (SN 11833) for routine measurement and another in 1982 (SN 21561) for "reference". A third pyranometer purchased in 1982 (SN 21560) is routinely used in another study ("WOOD" smoke) but is often used for comparison with the SN 11833 radiometer.

The Eppley Ultra-Violet Radiometer measures light of wavelengths from 290 to 385 nanometers. According to Eppley, "It is linear to better than plus or minus 2 percent over the normal operational range. Over a range of 90 to 10 degrees solar elevation, the mean deviation of instrument response from the ideal Lambert cosine law is in general, plus or minus 2 percent. Its response time is few milliseconds". The relative spectral response of the photocell is shown in Figure E1. The filters transmission characteristics are shown in Figure E2. One was purchased in 1972 (SN 12048) and another in 1982 (SN 21767) for use as a "reference". Supplied calibration factors expressed as mv/cal $cm^2$ $min^1$ (TSR) and mv/ mcal $cm^2$ $min^1$ (UV) are used to convert the millivolt signal to light data.

## General Description Of Light Measurement

The Quality Assurance factors for light data include: calibration of the radiometers, the accuracy of the time reported for collected data, the positioning of the radiometers to prevent shading, and the relationship between the light radiometer data, and the light reaching the chambers. Specific details are listed in later sections.

Initial calibrations were performed and supplied by the Eppley Laboratory at the time of purchase of the radiometers. Additional calibrations were performed by Eppley on several occaisions

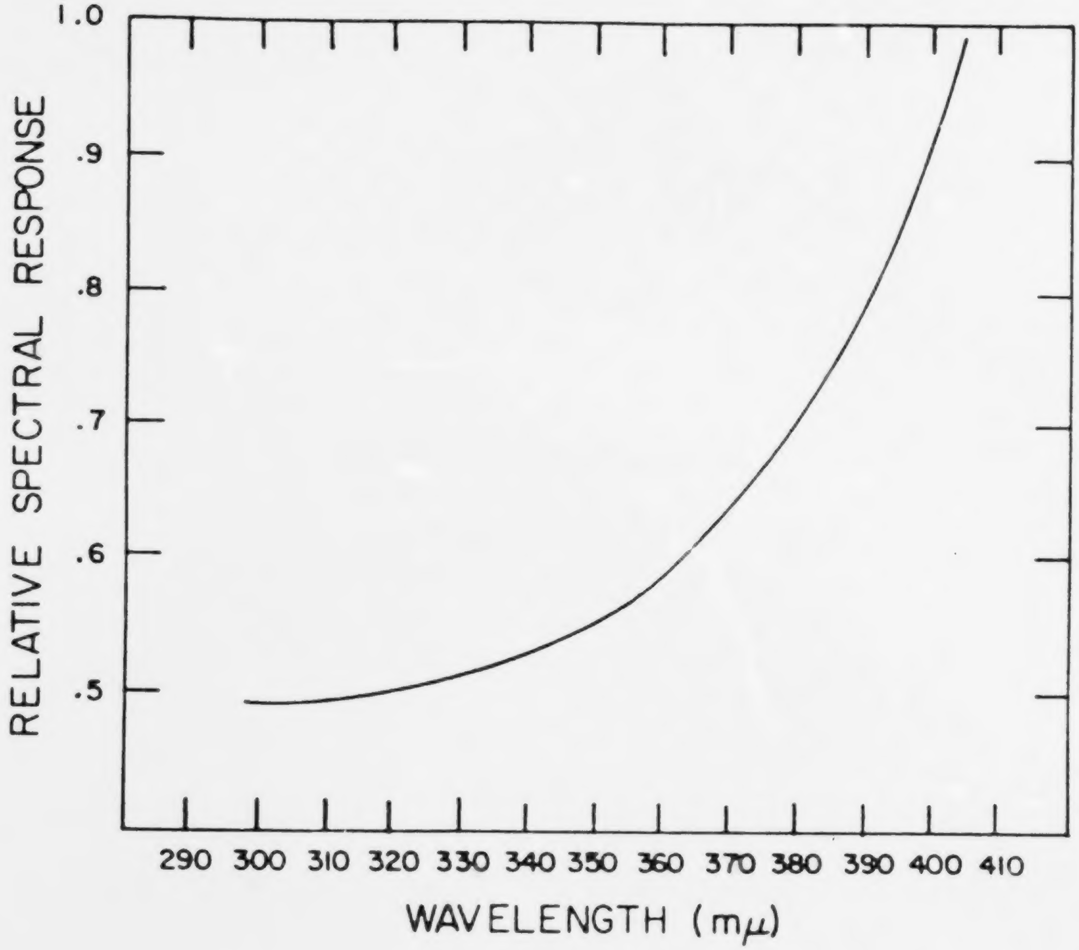


**Figure E1.** Relative Spectral Response of UV Photocell

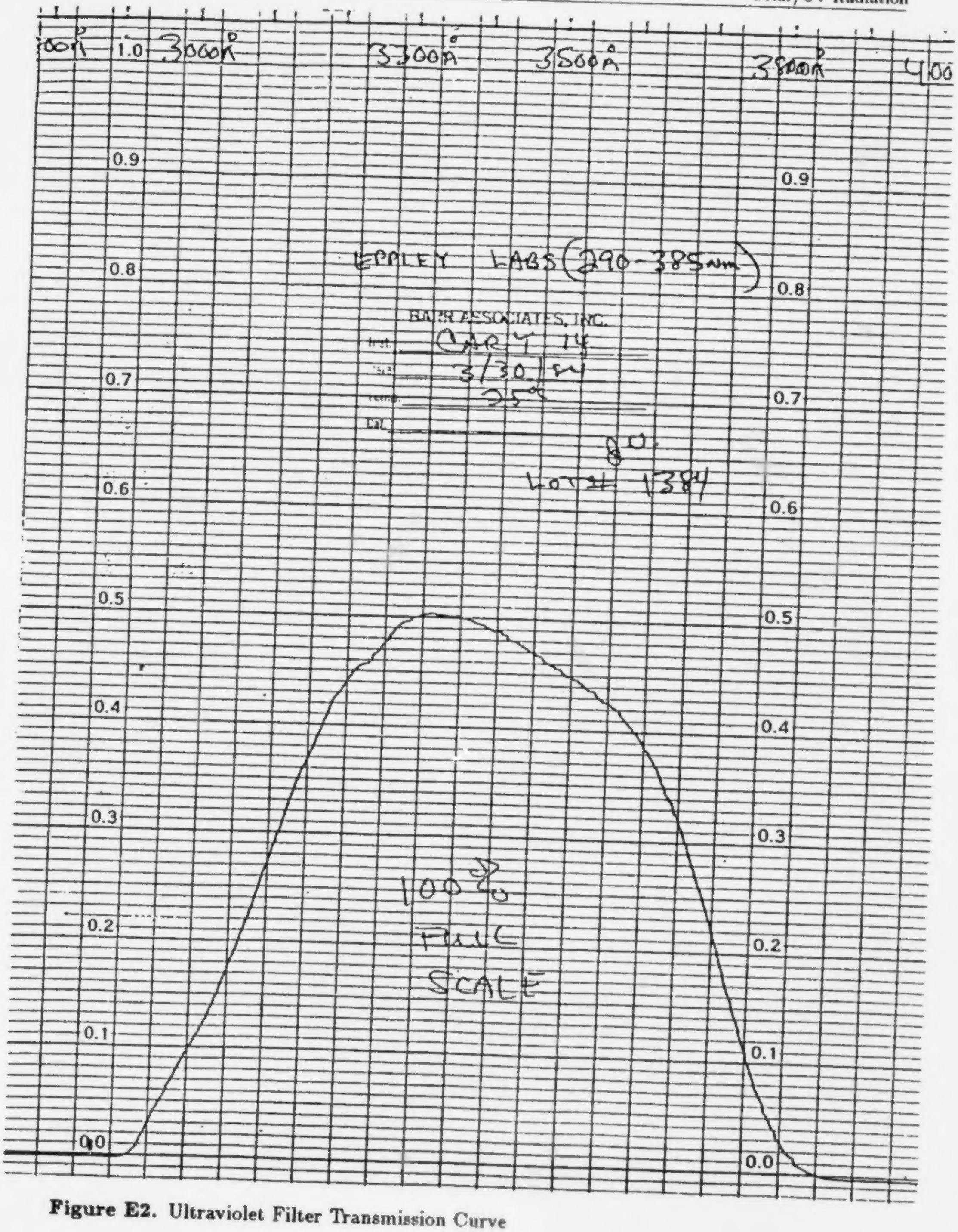


**Figure E2.** Ultraviolet Filter Transmission Curve

throughout the 10 year study period (see later table). In addition, comparison tests were routinely conducted by data processors to determine sensor stability. In these tests, measurements were compared between comparable days of different years to assess stability. Subsequent to obtaining additional radiometers, simultaneous comparisons between references and normal use radiometers were used to determine stability.

The radiometers output is recorded by an automated data-acquistion system (instantaneous every minute) and stripchart, continuously.

The official time, kept by computer clock was set by reference to a commercial time system telephone call.

The radiometers are mounted on a tower 25.7 feet above the ground (in 1974; far above trees). In later years (August 1983) trees were cut to minimize shading of the chambers at sunrise although there was no observed shading effect.

## General Operating Procedure

Two radiometers are placed on the tower at the beginning of the season (usually the spring). They are removed at the end of the season (usually the late fall) and stored indoors. The radiometers were used continuously through the winter of 1978/1979 and remained outdoors. Since the "reference" radiometers were purchased in 1982, they have been used for side-by-side comparisons as the "Tower" radiometers are installed and removed from the tower at the beginning and end of each experimental season.

## Radiometer And Calibration History

Until recently, UNC has depended on the calibrations performed at Eppley Laboratory Inc. UNC made comparisons with earlier collected data to insure that at least the responses were consistent from year to year for a given time on clear days. Calibrations are supplied from Eppley at time of purchase of the radiometers. The first two radiometers purchased in November 1972 were used without recalibration until 1980 for TSR and 1982 for UV. Year to year comparisons indicated problems in the 1980 and 1981 UV data, and 1979 and part of 1983 TSR data. The radiometers were sent to Eppley for recalibration, and in the spring of 1982, two new radiometers were purchased. These were reserved as references for quick comparisons with the original radiometers. Side-by-side comparisons provide a more precise check of instrument drift, than comparisons with past measurements. Recalibration has been performed several more times since 1980. The calibration history and calibration factors for all UNC light radiometers are listed in Table E1. These most recent calibrations have indicated that the first calibration supplied by Eppley for the UV radiometer was approximately 33 percent low. Comparisons with data obtained by the EPA division of Meteorology (Sickles[1], Rudisill[2] ) confirm this discovery.

## Calibration Procedures

Calibrations involve comparisons of radiometer output with other light radiometers. Comparisons performed by UNC are primarily used to confirm calibrations performed by Eppley Laboratory Inc. Before June 1985, Eppley calibrated UV radiometers with Eppley irradiance lamps calibrated

## Table E1. Eppley Calibration Factors And Dates

Part 1. The Total Solar Radiation Sensors. There are three sensors.

SN # 11833 GAS LAB

| mv/ langley/min | langley/min volt | eppley date | use start date | use end date | notes |
|---|---|---|---|---|---|
| 8.13 | 123.0 | 30-Nov-72 | 30-Nov-72 | 01-Feb-80 | |
| 8.07 | 123.9 | 01-Feb-80 | 01-Feb-80 | 14-May-84 | * |
| 8.11 | 123.3 | 14-May-84 | 14-May-84 | 11-Feb-86 | |
| 8.14 | 122.9 | 11-Feb-86 | 11-Feb-86 | 12-Nov-86 | |

* corrected for Eppley 2.6 percent

| | |
|---|---|
| ave | 123.2672 |
| std | 0.4072 |
| rel std | 0.33% |

SN # 21561 REFERENCE ''NEW GAS LAB 3-82''

| mv/ langley/min | langley/min volt | eppley date | use start date | use end date | notes |
|---|---|---|---|---|---|
| 7.18 | 139.3 | 16-Feb-82 | 16-Feb-82 | 12-Nov-86 | |

SN # 21560 WOOD LAB

| mv/ langley/min | langley/min volt | eppley date | use start date | use end date | notes |
|---|---|---|---|---|---|
| 7.30 | 137.0 | 11-Feb-82 | 11-Feb-82 | 12-Nov-86 | |

## Table E1cont. Eppley Calibration Factors And Dates

Part 2. The Eppley Ultraviolet Radiometer sensors. There are two sensors.

SN # 12048 GAS LAB

| mv/ mlangley/mi | mlangley/mi volt | eppley date | use start date | use end date | notes |
|---|---|---|---|---|---|
| 0.082 | 12195 | 03-Oct-72 | 03-Oct-72 | 05-Mar-82 | |
| 0.074 | 13514 | 05-Mar-82 | 05-Mar-82 | 14-May-84 | |
| 0.094 | 10638 | 14-May-84 | 14-May-84 | 01-Feb-85 | |
| 0.074 | 13441 | 01-Feb-85 | 00-Jan-00 | 00-Jan-00 | not used |
| 0.098 | 10204 | 12-Jun-85 | 12-Jun-85 | 07-Mar-86 | |
| 0.101 | 9901 | 07-Mar-86 | 07-Mar-86 | 12-Nov-86 | |

| | |
|---|---|
| ave | 11562 |
| std | 1398 |
| rel std | 12.1% |

SN # 21767 REFERENCE ''NEW GAS LAB 3-82''

| | mv/ mlangley/mi | mlangley/mi volt | eppley date | use start date | use end date | notes |
|---|---|---|---|---|---|---|
| | 0.153 | 6536 | 16-Feb-82 | 16-Feb-82 | 11-Feb-86 | |
| * | 0.145 | 6897 | 11-Feb-86 | 11-Feb-86 | 12-Nov-86 | |

* 4% change in Eppley NBS standard

| | | | |
|---|---|---|---|
| ave | 6716 | | |
| std | 180 | | |
| rel std | 2.68% | delta | 5.52% |

by comparisons with NBS standard irradiance lamps. Since June 1985, Eppley has used transfer standard radiometers of the same model calibrated directly with lamps obtained by the National Bureau of Standards. These calibrated light radiometers are placed side-by-side with the UNC radiometers outside for calibration.

W. J. Scholes of the Eppley Laboratory reports that their UV standard has changed three times since 1972 due to changes at NBS and because they were concerned for their aging lamp standard. These combined changes have resulted in some uncertainty of absolute calibrations (including questions over the direction of changes in the standards). The scale used by NBS was changed in 1973 resulting in a change of 4 percent (Daniels, Eppley Lab). A new standard in August of 1979 has associated with it an uncertainty of 8 percent which is carried through to current calibrations. Scholes reports that they "do not know" the direction (increase or decrease) in which the standard changed, only that it changed 8 percent. A new standard in June of 1985 had an absolute change of 4 percent due to changes at NBS; and although Eppley provides calibration factors with "2 percent accuracy" (Scholes), these still carry an 8 percent uncertainty from the earlier 1979 calibration standard.

The EPA division of Meteorology also used NBS standards to calibrate the radiometers used to gather data in the early mid-70's at Research Triangle Park (RTP), NC (30 km from the chamber site). We have used these EPA RTP data to compare with our site data. This data was also treated as calibration data (see next section).

Two changes in standard calibration procedures at Eppley also effect total solar radiation measurements with the pyranometers. According to Eppley literature, "In 1977, the calibration traceability of Eppley solar radiation measuring instruments has been changed from the International Pyrheliometric Scale of 1956 (IPS 1956) to the Absolute Scale (SI). This change based on the results of IPC IV is such that instruments calibrated in SI units yield irradiance values which are 2.1 percent higher than values which would be obtained using Eppley instruments calibrated previously and referenced to IPS."

Also, "On December 1, 1981, The Eppley Laboratory changed the values of the response of the standard pyranometers employed as the reference for transfer calibrations in the integrating hemisphere. This change was based on the latest realization of radiometric reference scale as embodied in the cavity pyrheliometer instruments and also on the results of recent national and international pyranometer comparisons".

Instruments calibrated prior to that date will have sensitivity values which are traceable to a number of intermediate radiation reference scales, but to the same transfer instrument. All previous sensitivity values are too high relative to the new scale which means that calculated radiation values are too low. Instruments calibrated between March 27, 1979 and December 1, 1981 should be adjusted by 2.6 percent in the sense that sensitivities should be lowered or irradiance values raised.

This adjustment for our 1980 Eppley calibration causes the agreement with the other three calibrations to be within 0.5 percent; all four calibrations have relative standard deviation of 0.3 percent.

## Uncertainty In Light Data

Uncertainty in the magnitude of reported light intensity data arise from uncertainties in the absolute response factors of the radiometers. In addition, the offset between our reported Eastern Daylight

Time measurements and the correct time used to relate solar time to chamber events hamper comparisons with theoretical photolytic rate constants. That is, our site clock was not always set to the correct EDT time.

## Absolute Light Measurements

The uncertainty of the response (calibration) factors is less for the TSR pyranometer than for the UV radiometers (W. Scholes, Eppley Laboratory). Flocchini[3] (UC-Davis) found in a five year, eight university DOE solar energy study that UV Eppley calibrations differed from NOAA calibrations on the average by 10 percent; concluding that the NOAA calibrations were more reliable. The calibration factor for the UV radiometer used at Georgia Tech. (participant) was adjusted 15 percent to agree with other radiometers used in the study (C.G. Justus, Georgia Tech.[4] ; R.G. Flocchini[3]).

Scholes at the Eppley Laboratory knows of this study and "does not disagree". He added that the uncertainty of the NBS lamp standard is 8 percent. The NBS standard was changed recently (within last 1.5 years) and our calibration factor reported in February 1986 (0.145) was actually indicating the same response of the radiometer last calibrated in 1982 with a factor of 0.153. Eppley reports however, that the TSR radiometers usually are very stable with no more than 1 percent change/year is normal.

Rudisill[2] of the EPA Division of Meteorology, RTP, NC has found similar differences between Eppley UV calibrations and NOAA NBS calibrations, describing the radiometer as "tempermental".

Comparisons of Rudisill's data from 1974 thru 1983 with our data can be used to correct earlier data. His radiometers showed excellent stability for several year; their calibration factors were eventually verified with calibrations performed at NOAA in Boulder. Such re-calibration results in all UNC UV data agreeing with recent Eppley UV calibrations based on "consistancy analysis" across years (solar noon maxima for a given time of year for all years were compared). There are some limitaions with this analysis technique however.

Perfectly clear days are rare. Apparently clear days often have less than 100 percent possible sun (days used for the consistency analysis were selected to insure at least 90 percent possible sun or have at least clear insolation periods at solar noon). The latter type of days sometimes have solar noon values between cloudy values are often as much as 3 percent higher than values on the clearest days. This is due to increased scattering and reflection from the surrounding clouds. UV scattering is known to increase more than visible in light under conditions of light cloud cover. However, even with these problems, the apparent consistency recognized within the "scatter" caused by non-ideal day data plus the apparent relativly good stability of the radiometer now gives us more confidence in the whole light database. Additional comparison data are being obtained.

Comparisons between UNC and Rudisill's data have been made for 40 clear-sky days (data available from both) from the years 1974 thru 1983. His data were used to to determine correction factors to earlier UNC data. Solar maxima for late June to early July and October were studied. The data were corrected with the factors listed in Table E2. Table E3 and Table E4 contain the data used in the consistency analysis. Table E5 shows the mean, standard and relative standard deviations, slope and standard error, intercept and standard error and the $r^2$ correlation. It can be seen that the slopes are very small (smaller than the standard error of estimate) and the $r^2$

correlation's are very small indicating virtually no relationship between solar noon maxima and time of the experimental program.

However, even with these problems, the apparent consistency recognized within the "scatter" caused by non-ideal day data plus the apparent relativly good stability of the radiometer now gives us more confidence in the whole light database. Additional comparison data are being obtained.

The two UV radiometers disagree by 10.2 percent. Part of this difference is due to the 4 percent change (decrease in intensity in June 1985) of Eppleys (NBS really) UV standard and calibration technique between the times these different instruments were last calibrated (see Table E6). The tower and "WOOD" pyranometers disagree by 5.6 percent and the "WOOD" and "reference" pyranometer disagree by [illegible].1 percent. The "WOOD" and "reference" pyranometers were each last calibrated in 1982 when they were purchased. The tower pyranometer was last calibrated more recently in 1984. Such comparisons perhaps may be useful in estimating the uncertainty of these measurements. The deviation of the calibration factors as determined by Eppley over time for a given instrument may also indicate the combined uncertainty of Eppley calibration procedures and any drift in response of an instrument over time. The "tower" UV radiometer (SN 12048) has been calibrated four times with a relative standard deviation of 11.3 percent. The "tower" TSR pyranometer (SN 11833) has been calibrated four times also with a relative standard deviation of 0.33 percent. It should be noted that one of the calibration factors for the UV radiometer performed by Eppley in February of 1985 was rejected after comparing side-by-side with our other UV radiometer. The instrument was returned to Eppley. Eppley claims that a loose wire inside was responsible for the odd measurements. No data was taken or processed with this "bad" calibration factor.

## Time and Solar Events

Although all collected data within a given day uses the same clock, the absolute solar time is needed when comparing theoretical light and photolysis rate calculations.

Some modelers use sunrise time to determine the time adjustment between astronomical calculations of solar events and the UNC clock. In the experimental data, sunrise time may seem to change inconsistently from day to day. This could be due to clock changes, or differences in the atmosphere (clouds, haze, smoke). Clock changes were infrequent however. Dew sometimes effects the amplitude of the earliest morning TSR data (but not UV).

There are several definitions of sunrise. The usual definition is the top of the sun at the horizon (center of sun at ZA = 90 deg, 50 min, Naval Observatory, 1984). The sky is light before this sunrise. Civilian twilight occurs earlier (ZA = 92 degrees). There are other definitions of twilight. Nautical twilight is defined as the zenith of 102 degrees, and the astronomical twilight as 108 degrees. The radiometer probably begins to respond somewhere between twilight and before actual sunrise. This may be as much as 30 minutes difference.

Before 1980, the laboratory clock had to be reset after a power failure. The official time was obtained from a commercial time telephone call. Beginning in the 1980 season a new clock (TCU-100 by Digital Pathways Inc.) was installed for use with the data acquisition and control software, with NiCad batteries capable of operating the clock for three months without power, with an accuracy of plus or minus 5 seconds per month. It was purposely made difficult to change the time of this clock: it was thought that it was better to keep the time consistent and make any needed time corrections later, rather than have operators possibly reseting the clock often.

## Table E2. Correction Factors To Be Applied To UNC Data

CORRECTION FACTORS FOR EPPLEY CALIBRATION FACTORS USED IN UNC DATA

| Date begin | Date end | TSR | UV | Comment |
|---|---|---|---|---|
| 30-Nov-72 | 31-Dec-73 | 1.00 | 1.50 | Eppley cal Nov-72 |
| 01-Jan-74 | 31-Dec-74 | 1.00 | 1.47 | |
| 01-Jan-75 | 12-Jun-76 | 1.00 | 1.54 | |
| 01-Jan-76 | 12-Jun-76 | 1.00 | 1.71 | |
| 13-Jun-76 | 31-Dec-76 | 1.00 | 1.54 | |
| 01-Jan-77 | 31-Dec-77 | 1.00 | 1.39 | |
| 01-Jan-78 | 31-Dec-78 | 1.00 | 1.38 | |
| 01-Jan-79 | 31-Dec-79 | 1.00 | 1.45 | |
| 01-Jan-80 | 14-Jun-80 | 1.00 | 1.55 | |
| 15-Jun-80 | 24-Jun-80 | 1.00 | 1.71 | response changes |
| 25-Jun-80 | 20-Jul-80 | 1.00 | 1.87 | |
| 21-Jul-80 | 30-Sep-80 | 1.00 | 2.20 | before repaired |
| 01-Oct-80 | 31-Dec-80 | 1.00 | 1.55 | |
| 01-Jan-81 | 31-Aug-81 | 1.00 | 1.70 | |
| 01-Sep-81 | 04-Mar-82 | 1.00 | 1.25 | |
| 05-Mar-82 | 31-Dec-82 | 1.00 | 1.00 ** | Eppley cal Mar-82 |
| 01-Jan-83 | 31-Dec-83 | 1.00 * | 1.00 ** | |
| 01-Jan-84 | 11-Jun-85 | 1.00 | 1.00 | Eppley cal May-84 |
| 12-Jun-85 | 06-Mar-86 | 1.00 | 1.00 | Eppley cal Jun-85 |
| 07-Mar-86 | 12-Nov-86 | 1.00 | 1.00 | Eppley cal Mar-86 |

from clearest days during this time period

* 1.28 was used in dataprocessing to correct TSR data
** 1.108 should be applied to UV data of 1982-83 experiments processed before 1986

UV correction values from comparison with Rudisill's radiometers (EPA, Div. of Meteorology)

## Table E3. Solar Maxima for June and July

| date | tsr | uv | tsr*f | uv*f | uv/tsr |
|---|---|---|---|---|---|
| 02-Jun-73 | 1.4576 | 42.44 | 1.4576 | 63.66 | 4.37% |
| 22-Jul-73 | 1.3653 | 45.49 | 1.3653 | 68.23 | 5.00% |
| 24-Jul-73 | 1.6002 | 52.08 | 1.6002 | 78.12 | 4.88% |
| 11-Jun-74 | 1.3382 | 48.54 | 1.3382 | 71.21 | 5.32% |
| 18-Jun-74 | 1.3284 | 46.20 | 1.3284 | 67.78 | 5.10% |
| 25-Jun-74 | 1.4576 | 48.17 | 1.4576 | 70.68 | 4.85% |
| 02-Jun-75 | 1.4403 | 48.78 | 1.4403 | 75.30 | 5.23% |
| 03-Jun-75 | 1.5141 | 47.32 | 1.5141 | 73.04 | 4.82% |
| 04-Jun-75 | 1.3481 | 48.66 | 1.3481 | 75.11 | 5.57% |
| 14-Jun-75 | 1.3296 | 47.93 | 1.3296 | 73.98 | 5.56% |
| 15-Jun-75 | 1.3924 | 47.32 | 1.3924 | 73.04 | 5.25% |
| 26-Jul-75 | 1.2960 | 44.51 | 1.2960 | 68.71 | 5.30% |
| 06-Jun-76 | 1.3520 | 43.54 | 1.3520 | 74.49 | 5.51% |
| 08-Jun-76 | 1.3260 | 40.61 | 1.3260 | 69.48 | 5.24% |
| 18-Jun-76 | 1.4220 | 48.54 | 1.4220 | 74.57 | 5.24% |
| 24-Jun-76 | 1.4020 | 46.22 | 1.4020 | 71.01 | 5.06% |
| 25-Jun-76 | 1.4440 | 46.46 | 1.4440 | 71.38 | 4.94% |
| 13-Jul-76 | 1.3280 | 48.29 | 1.3280 | 74.19 | 5.59% |
| 03-Jun-77 | 1.4400 | 53.17 | 1.4400 | 73.87 | 5.13% |
| 10-Jun-77 | 1.3810 | 52.68 | 1.3810 | 73.19 | 5.30% |
| 21-Jun-77 | 1.3600 | 50.98 | 1.3600 | 70.82 | 5.21% |
| 29-Jun-77 | 1.3900 | 53.05 | 1.3900 | 73.70 | 5.30% |
| 18-Jul-77 | 1.2927 | 45.73 | 1.2927 | 63.53 | 4.91% |
| 27-Jul-77 | 1.3260 | 52.07 | 1.3260 | 72.34 | 5.46% |
| 01-Jun-78 | 1.4370 | 51.22 | 1.4370 | 70.51 | 4.91% |
| 10-Jun-78 | 1.3300 | 50.37 | 1.3300 | 69.33 | 5.21% |
| 16-Jun-78 | 1.3580 | 46.59 | 1.3580 | 64.14 | 4.72% |
| 19-Jun-78 | 1.2820 | 47.32 | 1.2820 | 65.14 | 5.08% |
| 21-Jul-78 | 1.2930 | 49.87 | 1.2930 | 68.65 | 5.31% |
| 22-Jul-78 | 1.3010 | 50.00 | 1.3010 | 68.83 | 5.29% |
| 30-Jul-78 | 1.3616 | 46.46 | 1.3616 | 63.96 | 4.70% |
| 09-Jun-79 | 0.8650 | 48.42 | 1.2110 | 70.03 | 5.78% |
| 12-Jun-79 |  | 52.50 |  | 75.94 |  |
| 13-Jun-79 | 0.9420 | 49.88 | 1.3188 | 72.15 | 5.47% |
| 20-Jun-79 | 0.9729 | 53.29 | 1.3621 | 77.09 | 5.66% |

## Table cont. E3. Solar Maxima for June and July

| date | tsr | uv | tsr*f | uv*f | uv/tsr |
|---|---|---|---|---|---|
| 26-Jun-79 | 0.9420 | 51.59 | 1.3188 | 74.62 | 5.66% |
| 03-Jul-79 | 1.0120 | 51.83 | 1.4168 | 74.97 | 5.29% |
| 06-Jul-79 | 1.1090 | 56.10 | 1.5526 | 81.15 | 5.23% |
| 04-Jun-80 | 1.4180 | 44.63 | 1.4180 | 69.18 | 4.88% |
| 27-Jun-80 | 1.4770 | 40.90 | 1.4770 | 76.44 | 5.18% |
| 14-Jul-80 | 1.4010 | 36.60 | 1.4010 | 68.41 | 4.88% |
| 16-Jul-80 | 1.3850 | 34.00 | 1.3850 | 63.55 | 4.59% |
| 20-Jul-80 | 1.4800 | 38.50 | 1.4800 | 71.96 | 4.86% |
| 30-Jul-80 | 1.4034 | 31.71 | 1.4034 | 69.76 | 4.97% |
| 29-Jun-81 | 1.6013 |  | 1.6013 | 71.34 | 4.46% |
| 15-Jul-81 | 1.3826 | 43.48 | 1.3826 | 73.85 | 5.34% |
| 21-Jul-81 | 1.4780 | 42.40 | 1.4780 | 72.02 | 4.87% |
| 22-Jul-81 | 1.4500 | 42.90 | 1.4500 | 72.87 | 5.03% |
| 02-Jun-82 | 1.4400 | 64.30 | 1.4400 | 71.25 | 4.95% |
| 08-Jul-82 | 1.4360 | 61.22 | 1.4360 | 67.84 | 4.72% |
| 17-Jul-82 | 1.5495 | 66.95 | 1.5495 | 74.19 | 4.79% |
| 01-Jul-82 | 1.3949 | 64.63 | 1.3949 | 71.62 | 5.13% |
| 08-Jul-82 | 1.3901 | 64.76 | 1.3901 | 71.76 | 5.16% |
| 10-Jun-83 | 1.4990 | 64.90 | 1.4990 | 71.92 | 4.80% |
| 12-Jun-83 | 1.4060 | 66.20 | 1.4060 | 73.36 | 5.22% |
| 23-Jun-83 | 1.3937 | 77.30 | 1.3937 | 77.30 | 5.55% |
| 07-Jul-83 | 1.4042 | 66.00 | 1.4042 | 73.14 | 5.21% |
| 08-Jul-83 | 1.4222 | 67.20 | 1.4222 | 74.46 | 5.24% |
| 09-Jul-83 | 1.3882 | 66.83 | 1.3882 | 74.05 | 5.33% |
| 13-Jul-83 | 1.3786 | 61.70 | 1.3786 | 68.37 | 4.96% |
| 14-Jul-83 | 1.4042 | 63.40 | 1.4042 | 70.25 | 5.00% |
| 27-Jul-83 | 1.3728 | 64.63 | 1.3728 | 71.62 | 5.22% |
| 26-Jun-84 | 1.5068 | 75.21 | 1.5068 | 75.21 | 4.99% |
| 11-Jul-84 | 1.3900 | 67.26 | 1.3900 | 67.26 | 4.84% |
| 26-Jun-85 | 1.4402 | 66.41 | 1.4402 | 66.41 | 4.61% |
| 28-Jun-85 | 1.4408 | 65.82 | 1.4408 | 65.82 | 4.57% |
| 08-Jul-85 | 1.4303 | 66.33 | 1.4303 | 66.33 | 4.64% |

## Table E4. Solar Maxima for October

| date | tsr | uv | tsr*f_oc | uv*f_oc | uv/tsr_oc |
|---|---|---|---|---|---|
| 17-Oct-73 | 1.0381 | 34.51 | 1.0381 | 51.77 | 4.99% |
| 20-Oct-73 | 0.9631 | 30.37 | 0.9631 | 45.55 | 4.73% |
| 22-Oct-73 | 0.9385 | 29.76 | 0.9385 | 44.63 | 4.76% |
| 03-Oct-74 | 1.1156 | 38.41 | 1.1156 | 56.36 | 5.05% |
| 04-Oct-74 | 1.1008 | 37.56 | 1.1008 | 55.11 | 5.01% |
| 05-Oct-74 | 1.0812 | 36.46 | 1.0812 | 53.50 | 4.95% |
| 06-Oct-74 | 1.1205 | 35.98 | 1.1205 | 52.78 | 4.71% |
| 22-Oct-74 | 1.0024 | 32.68 | 1.0024 | 47.95 | 4.78% |
| 23-Oct-74 | 0.9766 | 31.46 | 0.9766 | 46.16 | 4.73% |
| 13-Oct-75 | 1.0300 | 33.66 | 1.0300 | 51.96 | 5.04% |
| 15-Oct-75 | 0.9950 | 31.95 | 0.9950 | 49.32 | 4.96% |
| 21-Oct-75 | 0.9740 | 30.98 | 0.9740 | 47.82 | 4.91% |
| 06-Oct-76 | 1.1480 | 35.49 | 1.1480 | 54.52 | 4.75% |
| 11-Oct-76 | 1.1760 | 33.90 | 1.1760 | 52.08 | 4.43% |
| 12-Oct-76 | 1.0340 | 33.70 | 1.0340 | 51.77 | 5.01% |
| 13-Oct-76 | 0.9770 | 31.59 | 0.9770 | 48.52 | 4.97% |
| 15-Oct-76 | 1.1180 | 30.85 | 1.1180 | 47.40 | 4.24% |
| 18-Oct-76 | 1.0430 | 34.39 | 1.0430 | 52.83 | 5.07% |
| 23-Oct-76 | 0.9980 | 31.34 | 0.9980 | 48.15 | 4.82% |

## Table cont. E4. Solar Maxima for October

| date | tsr | uv | tsr*f | uv*f | uv/tsr |
|---|---|---|---|---|---|
| 20-Oct-77 | 0.8780 | 35.37 | 0.8780 | 49.14 | 5.60% |
| 22-Oct-77 | 0.9930 | 34.00 | 0.9930 | 47.24 | 4.76% |
| 02-Oct-78 | 1.0890 | 38.90 | 1.0890 | 53.55 | 4.92% |
| 10-Oct-78 | 1.0650 | 37.07 | 1.0650 | 51.04 | 4.79% |
| 18-Oct-78 | 1.0180 | 35.00 | 1.0180 | 48.18 |  |
| 20-Oct-78 | 1.0295 | 35.61 | 1.0295 | 49.02 | 4.76% |
| 21-Oct-78 | 0.9720 | 32.93 | 0.9720 | 45.33 | 4.66% |
| 25-Oct-78 | 0.9770 | 33.29 | 0.9770 | 45.83 | 4.69% |
| 20-Oct-78 | 1.0295 | 35.61 | 1.0295 | 49.02 | 4.76% |
| 03-Oct-79 | 0.7380 | 37.68 | 1.0332 | 54.51 | 5.28% |
| 06-Oct-79 | 0.7320 | 37.81 | 1.0248 | 54.69 | 5.34% |
| 14-Oct-79 | 0.7020 | 35.49 | 0.9828 | 51.33 | 5.22% |
| 20-Oct-79 | 0.7552 | 33.78 | 1.0573 | 48.86 | 4.62% |
| 24-Oct-79 | 0.6630 | 33.17 | 0.9282 | 47.98 | 5.17% |
| 31-Oct-79 | 0.6610 | 29.51 | 0.9254 | 42.69 | 4.61% |
| 07-Oct-80 | 1.1670 | 30.40 | 1.1670 | 47.12 | 4.04% |
| 03-Oct-81 | 1.1930 | 42.20 | 1.1930 | 52.75 | 4.42% |
| 14-Oct-81 | 1.0664 | 37.80 | 1.0664 | 47.26 | 4.43% |
| 28-Oct-81 | 0.9960 | 33.50 | 0.9960 | 41.88 | 4.20% |
| 01-Oct-82 | 1.1582 | 49.27 | 1.1582 | 54.59 | 4.71% |
| 19-Oct-82 | 0.9780 | 41.60 | 0.9780 | 46.10 | 4.71% |
| 27-Oct-82 | 0.9517 | 39.88 | 0.9517 | 44.19 | 4.64% |
| 06-Oct-83 | 1.1115 | 50.61 | 1.1115 | 56.08 | 5.05% |
| 04-Oct-84 | 1.1147 | 52.13 | 1.1147 | 52.13 | 4.68% |
| 09-Oct-85 | 1.1467 | 51.02 | 1.1467 | 51.02 | 4.45% |

## Table E5. Summary of Comparison

| Sensor/Seas | Obs | Mean | Std | Rel Dev |
|---|---|---|---|---|
| TSR/ SUMMER | 66 | 1.401 | 0.074 | 5.27% |
| TSR/ FALL | 44 | 1.039 | 0.075 | 7.22% |
| UV/ SUMMER | 67 | 71.34 | 3.75 | 5.25% |
| UV/ FALL | 44 | 49.77 | 3.64 | 7.32% |

| Sensor/Seas | Obs | slope | Std Err | intrcpt | Std Err | r2 |
|---|---|---|---|---|---|---|
| TSR/ SUMMER | 66 | 4.67E-03 | 5.27E-03 | 1.335 | 0.143 | 0.012 |
| TSR/ FALL | 44 | 6.06E-03 | 3.68E-03 | 1.078 | 0.075 | 0.044 |
| UV/ SUMMER | 67 | 0.064 | 0.140 | 70.16 | 3.80 | 0.002 |
| UV/ FALL | 44 | 0.178 | 0.183 | 48.45 | 3.72 | 0.001 |

| | TSR | UV | UV/TSR |
|---|---|---|---|
| AVG June,Ju | 1.4006 | 71.34 | 5.11% |
| STD June,Ju | 0.0738 | 3.75 | 0.30% |
| | 5.27% | 5.25% | |
| AVG Oct | 1.0390 | 49.77 | 4.80% |
| STD Oct | 0.0750 | 3.64 | 0.30% |
| | 7.22% | 7.32% | |
| AVG ALL UV | | | 4.99% |
| STD ALL UV | | | 0.34% |

## Table E6. Side-by-Side Radiometer Comparisons

```
TSR
11833/21561 av sig ratio        "GAS" TO "REF"
SIDE BY SIDE COMPARISONS OF SENSORS WITH CHART CALS (av output)

5/16 recorder check 20 MV SCALE GOOD - NO CORRECTION NEEDED'

      DATE
             10.92       9.2      10.5                                       ave       std    SN MV/LANG
              9.44       7.7      9.06
5/16        1.1568    1.1940    1.1589                                    1.1702    0.0174     11833      8.11
              11.8     12.88      10.9      12.2      11.6       2.8
              9.87     10.85       8.4      10.3       9.9       2.4
5/20        1.1955    1.1871    1.2976    1.1845    1.1717    1.1667    1.2005    0.0445     21561      7.18
               9.2      9.56      8.99      9.38
               7.6      7.83       7.3       7.6
7/31        1.2105    1.2209    1.2315    1.2342                        1.2210    0.0086 11833/21561    1.13

                                                               AVG    1.1972    0.0235
                                                               STD    0.0209
                                                           REL STD      1.7%
                                                                                            OBSERVED
                                                                                                1.20

                                                                                            DELTA
TSR                                                                                            -6.0%
21560/21561 av sig ratio        "WOOD" TO "REF"       PERFORMED INSIDE WOOD CHAMBERS
SIDE BY SIDE COMPARISONS OF SENSORS


      DATE
              8.39      6.95                                                 ave       std    SN MV/LANG
              8.29      6.87
8/22        1.0121    1.0116                                          1.0119    0.0002     21560       7.3
              3.35      2.55      4.15      3.65
              3.15       2.5      4.04      3.55
8/24        1.0635    1.0200    1.0272    1.0282                      1.0347    0.0169
              6.65      7.65       5.8                                                     21561      7.18
              6.45      7.35       5.5
9/3         1.0310    1.0408    1.0545                                1.0359    0.0049 21560/21561  1.0167

                                                               AVG    1.0275    0.0073
                                                               STD    0.0111
                                                           REL STD      1.1%
                                                                                          ' OBSERVED
                                                                                              1.0275

                                                                                            DELTA
                                                                                               -1.1%

UV        21767/12048                                                  SN               MV/LANG
SIDE BY SIDE COMPARISONS OF SENSORS WITH CHART CALS (av output)     21767                    0.153
7/31 true      0.008    0.0038    0.0012                            12048                    0.098
      rec    0.00804   0.00387   0.00122
true/rec      0.9950    0.9819    0.9836       avg    0.9868
                                                                    21767/12048               1.56
5/16 cal                                       avg    0.9889
5/20 true     0.0097                                                                 OBSERVED
      rec     0.0098                                                                     1.40
true/rec      0.9898                           avg    0.9898
                                                                                     DELTA
      DATE       AVE                                                                    10.2%
"21767"                 6.1000    6.0900    5.6400    6.2050
"12048"                 4.3421    4.3323    4.0559    4.4161
      7/31    1.4015    1.4048    1.4057    1.3906    1.4051

Sensor sent back to Eppley May 29, 1985


"21767"                 8.6400
"12048"                 6.7937
      5/16    1.2718    1.2718

"21767"                 6.7306    6.8000              AVE    1.2665
"12048"                 5.3000    5.4290              STD    0.0638
      5/20    1.2612    1.2699    1.2525          REL STD      5.04%
```

For data processing, sunrise was determined by inspection of the light data and reporting the time that a non-zero light reading was recorded. Observations at the Site at sunrise by many experimental operators have been that light enough to walk about without flashlights is required to produce a response in the radiometers. The sun is not directly visible at this time. One recommended technique is to use a high quality astronomical program to calculate true solar noon for a specific day and site location and to compare clear day TSR with symmetry around this solar noon time.

## Albedo And Local Topography

The chamber site is a rural area surrounded by mostly pine trees. There are only a few local residences (mostly north and northwest) and the road receives little traffic. Nearby small fields are used only for hay producing.

The area is generally flat yet the topography effecting sunrise and higher elevations at sunset may need to be considered when comparing theoretical sunrise and sunset times with experimental data (see Figure E3: a portion of the topographical map). The elevation of the site is 340 feet. The elevation of the hill (with a residence) to the southwest is 372 feet (about 500-600 feet away). The elevation to the east falls to 310 feet at approximately 500 feet from the site then increases to 370-380 about 1500 feet further. To the south the land remains at roughly the same elevation except for a revine 1000 feet away southsoutheast which is roughly 50 feet lower. There are very few hills within a mile of the site which are higher than 400 feet. The location of the smog chamber site is latitude 35.71 degrees north, longitude 79.11 degrees west. The magnetic correction to true north has varied from +4 degrees in 1974 to +6.5 degrees in 1981; it is now +6 degrees (1986, from aviation map). The long axis of the chamber runs North-east to southwest 30 degrees off of the magnetic north. Therefore the chamber points 36 degrees east of true geographical north.

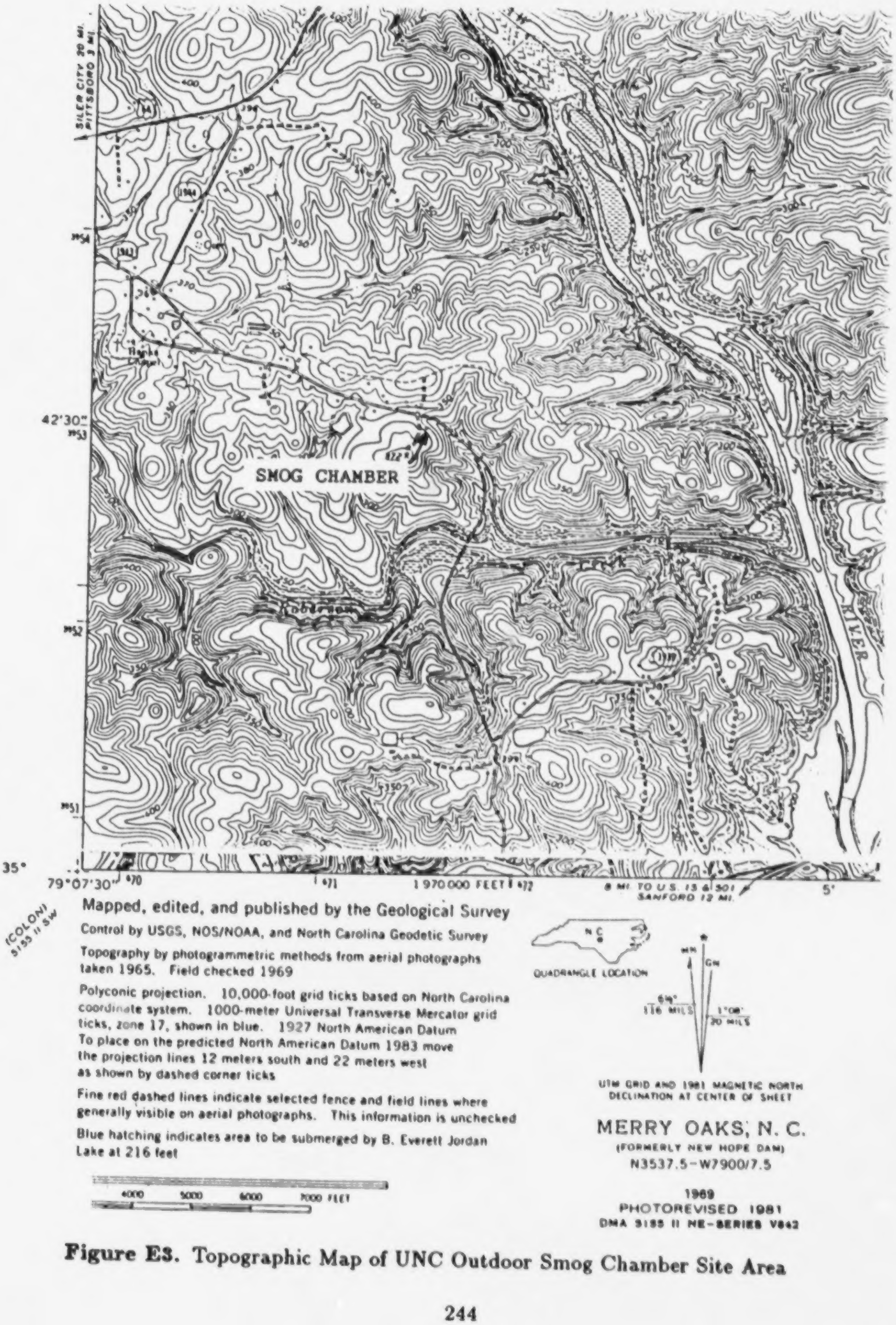
## Position Of Radiometers

The radiometers are mounted to a rigid wooden board (4" x 4"), leveled, on a tower 25.7 feet above the ground. The mounting board is parallel to the chamber. The radiometers are mounted 40 inches from each other (20 inches each from the center of the tower. The tower is located on the "southernly" side of the laboratory, 70 feet "westerly" and 7.9 feet "south" from a line perpendicular from the long axis of the chamber. The smog chamber is 21.5 feet tall 5 (from the ground); the ridge cover adds another 1.5 feet.

## Sun Path, Trees And Chamber Structure Shading

The surrounding trees have grown approximately 27 feet since 1974. The trees in the winter of 1985/86 are approximately 42 to 45 feet tall (northeast and southwest sides of chamber). The northeast tree line is perpendicular to the long chamber axis, 79 feet from the center of the chamber at the closest point. The southwest trees are generally also in a perpendicular line 69 feet from the center of the chamber at the closest point. Shorter trees (about 22 feet tall) to the east 150 feet from the chamber center are in a line parallel to the long axis of the chamber.

Detailed location and size measurements of the buildings, chambers, and trees have been made and analyzed in 3-dimension projection computer programs with input from an astronomical solar position program[5] to investigate shading and reflection effects on the chamber. Example pictures


SILER CITY 20 MI.
PITTSBORO 3 MI.
SMOG CHAMBER
RIVER
Robeson
42'30"
35°
79°07'30"
470
471
1 970 000 FEET
472
8 MI. TO U.S. 15 & 501
SANFORD 12 MI.
5'
(COLON)
5155 II SW
QUADRANGLE LOCATION
N C
MN
GN
6¼°
116 MILS
1°08'
20 MILS
4000
5000
6000
7000 FEET

Mapped, edited, and published by the Geological Survey

Control by USGS, NOS/NOAA, and North Carolina Geodetic Survey

Topography by photogrammetric methods from aerial photographs taken 1965. Field checked 1969

Polyconic projection. 10,000-foot grid ticks based on North Carolina coordinate system. 1000-meter Universal Transverse Mercator grid ticks, zone 17, shown in blue. 1927 North American Datum
To place on the predicted North American Datum 1983 move the projection lines 12 meters south and 22 meters west as shown by dashed corner ticks

Fine red dashed lines indicate selected fence and field lines where generally visible on aerial photographs. This information is unchecked

Blue hatching indicates area to be submerged by B. Everett Jordan Lake at 216 feet

UTM GRID AND 1981 MAGNETIC NORTH
DECLINATION AT CENTER OF SHEET

MERRY OAKS, N. C.
(FORMERLY NEW HOPE DAM)
N3537.5–W7900/7.5

1969
PHOTOREVISED 1981
DMA 5155 II NE–SERIES V842

**Figure E3.** Topographic Map of UNC Outdoor Smog Chamber Site Area

and output are shown in Figure E4, Figure E5, and Figure E6. Sky-view projections (horizon) have been measured and determined for 1976 and 1985 (Figure E7). These can be compared to the detailed sun-path projections for different seasons of the year in Figure E8.

## Data Acquisition

Two types of data acquisition are used for light data. The computer controlled system takes and records instantaneous readings every minute, where usually only the fourth minute is reported along with the other regular 4 minute data. A high accuracy 5 1/2 digit Hewlett Packard digital voltmeter is used. For most years these minute instantaneous readings are printed as the data are taken. The data are recorded continuously also on stripchart for many later years. The HP digital voltmeter is also used to calibrate the stripchart recorders.

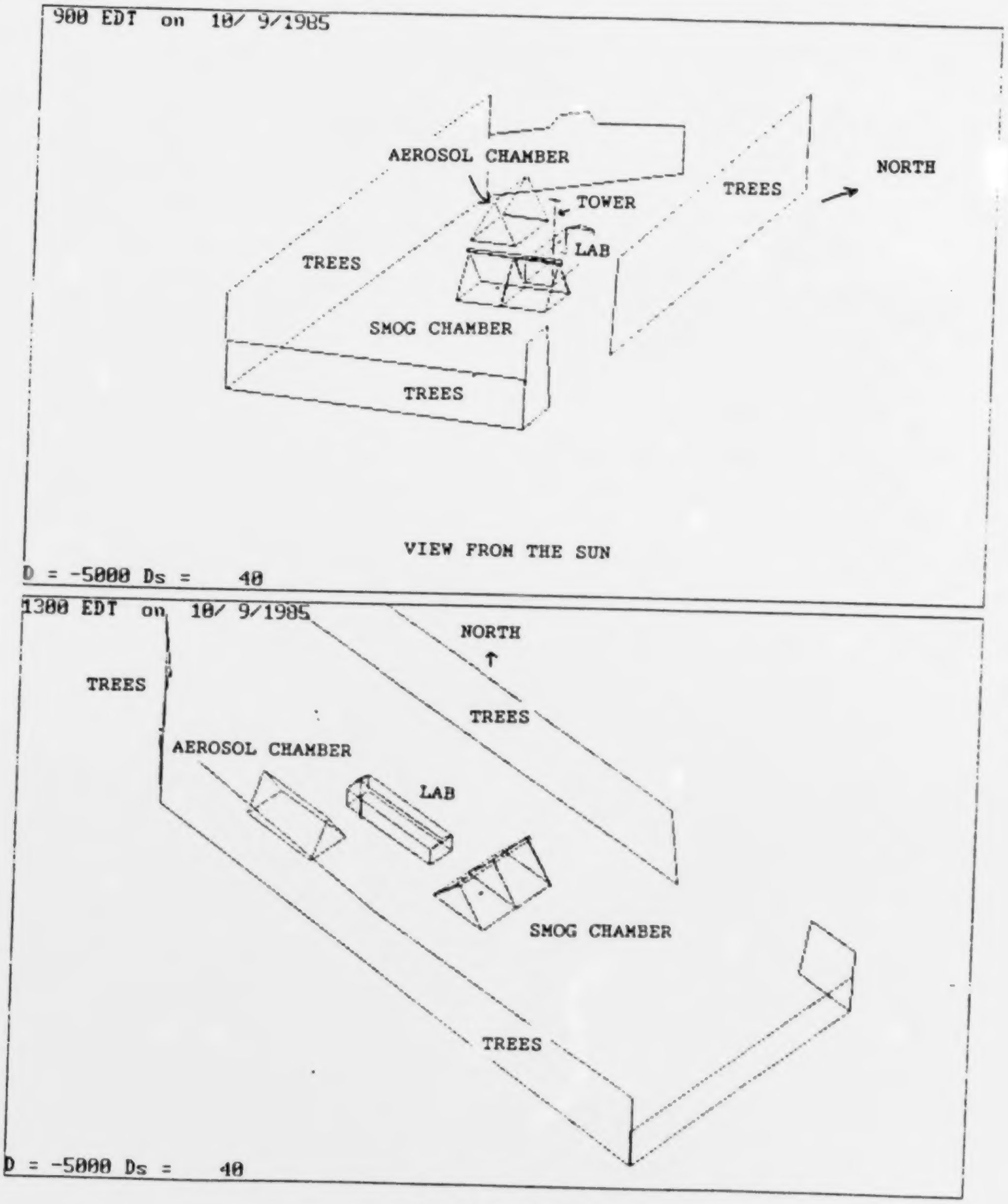
## Correction Factors For UNC Light Data

Correction factors for UNC TSR and UV data distributed in SEGFILES before 1986 are listed in Table E2. These were determined by listing solar noon maximum readings of TSR and UV for both midsummer and October for all years, comparing with readings from more recent calibrations from Eppley and from calibrations and data taken in 1974 thru 1983 at the EPA Division of Meteorology (citeref2). The UV/TSR ratio was calculated and used to help validate the measurements since the TSR radiometer is reportedly more stable. A least squares fit and regression were determined. See Figure E9 to E13. No long term trends are indicated. The data used from Rudisill's study are shown in Figure E14 and also with the June and July data in Figure E15.

Variations of solar noon maxima between apparently clear days have been observed. This is due in part to slight differences in the atmosphere. For example Demerjian shows column O3 changes throughout the season which will affect the UV more than the visible radiation. Ernie Goldberg of the Smithsonian's Environmental Research Center, (Rockville, MD) has indicated that variations of plus or minus 5 percent have been observed and can be effected by a number of causes such as urban pollution, or plant (biological) activity (eg pollen). Ozone column data taken at Nashville, Tennessee have been ordered and will be processed for future use.

The TSR pyranometer has been very stable, requiring no correction during this period except for 1979 (response low) and after June for the 1983 season (response low, increased by 28 percent in data processing) when water penetrated the sealed pyranometer. The UV radiometer response factor appears to have been stable from 1972 to June 1980, and after 1981. Before 1980, the UV data should be increased by the factors listed in Θcorrunc. No correction of data appears necessary after 1981. Inspection of all UV data collected in the summer of 1980 indicate that the radiometer response decayed quickly within a 6 week period at a steady rate. Increasing correction factors can be applied to periods within this time period. Other than this period, no strong trends are indicated in this 12 years of data.

In addition to problems with the radiometer calibration factors, errors occured in the application of given and accepted calibration factors for the 1982 and 1983 UV data. The older calibration factor was applied instead of the new factor. The reported data processed in SEGFILES distributed before 1986 need to be increased by 1.108 for run conducted in 1982 and 1983. 1984 data were processed with the proper calibratin factors. As a rule of thumb, UV solar noon maxima for late June on clear days will be in the mid 70's mcal $cm^{-2}$ $min^{-1}$ and TSR will be 1.4–1.6 cal $cm^{-2}$ $min^{-1}$.


900 EDT on 10/ 9/1985
AEROSOL CHAMBER
TOWER
LAB
TREES
NORTH
TREES
SMOG CHAMBER
TREES
VIEW FROM THE SUN
D = -5000 Ds = 40
1300 EDT on 10/ 9/1985
NORTH
TREES
TREES
AEROSOL CHAMBER
LAB
SMOG CHAMBER
TREES
D = -5000 Ds = 40

VIEW FROM THE SUN

**Figure E4.** Sun View of Research Site at Selected Times

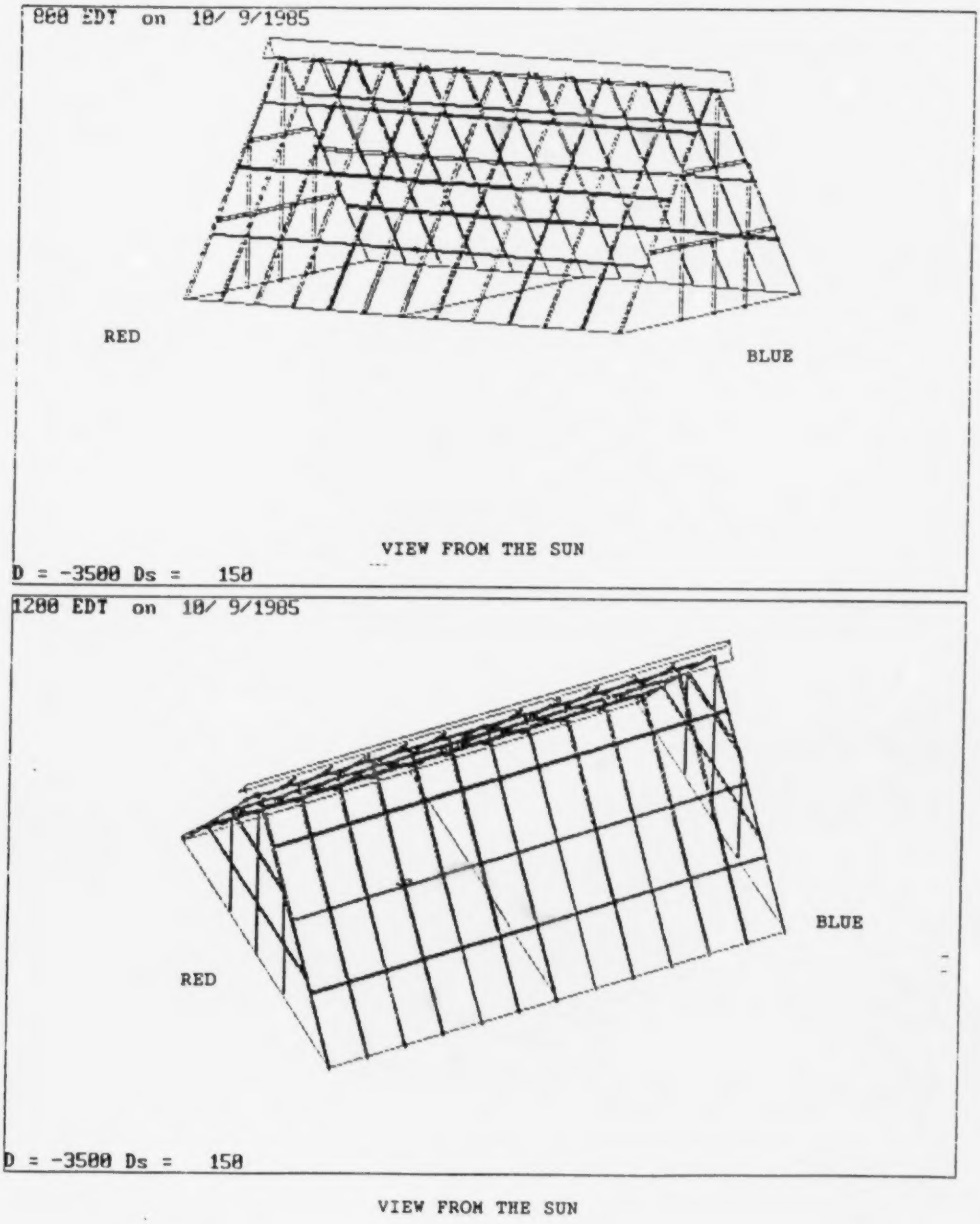

800 EDT on 10/ 9/1985
RED
BLUE
VIEW FROM THE SUN
D = -3500 Ds = 150
1200 EDT on 10/ 9/1985
BLUE
RED
D = -3500 Ds = 150
VIEW FROM THE SUN

**Figure E5.** Sun View of Smog Chamber at Selected Times

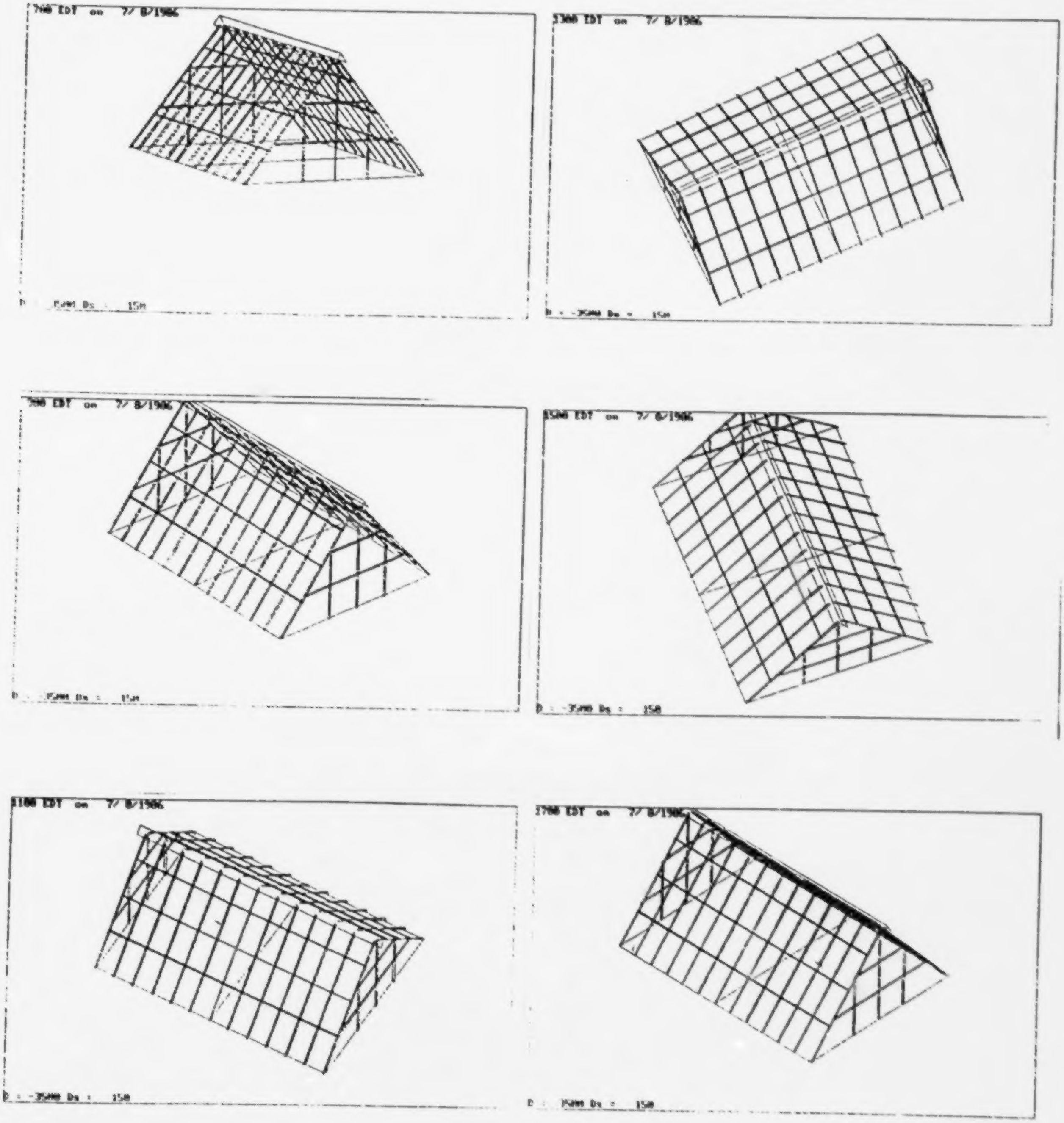

700 EDT on 7/ 8/1986
D : -3500 Ds : 150
1300 EDT on 7/ 8/1986
D = -3500 Ds = 150
900 EDT on 7/ 8/1986
D : -3500 Ds : 150
1500 EDT on 7/ 8/1986
D : -3500 Ds : 150
1100 EDT on 7/ 8/1986
D : -3500 Ds : 150
1700 EDT on 7/ 8/1986
D : -3500 Ds : 150

**Figure E6.** Sun View of Smog Chamber at Each Hour for July 8

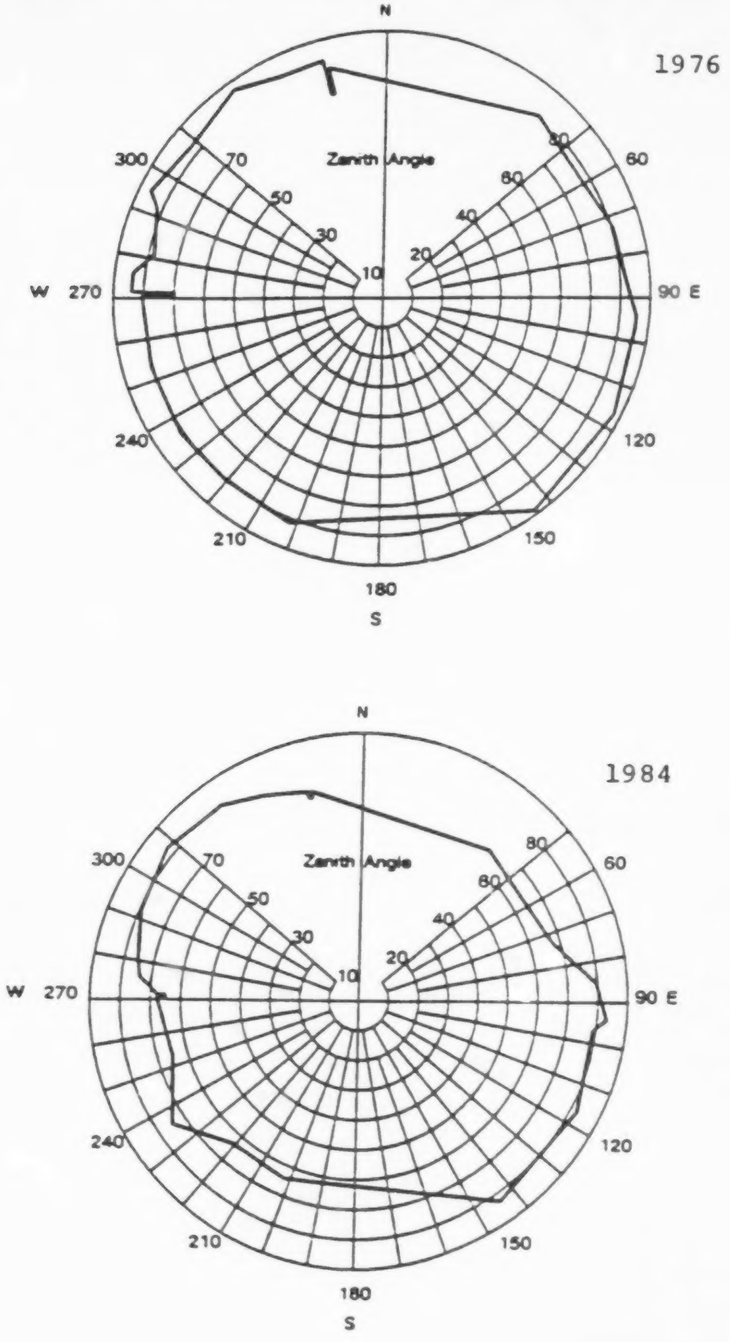
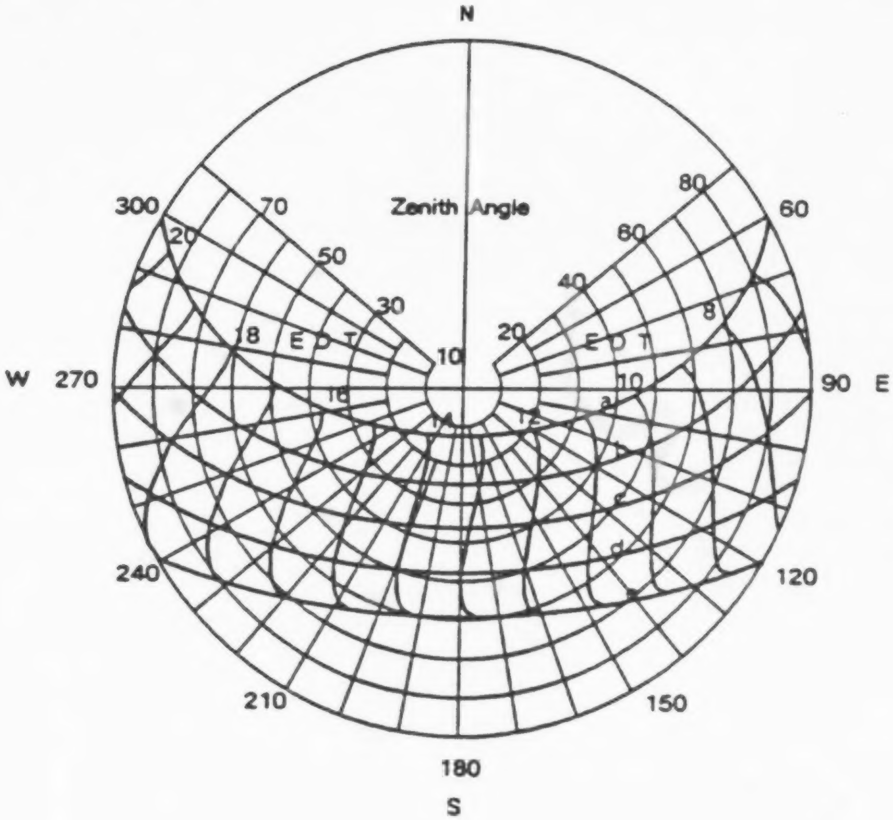


**Figure E7.** Research Site Horizon and Sky-view Projections



a- June 22, b-August 24, c-September 23
d-October 24, e-December 22

**Figure E8.** Path of Sun at Research Site

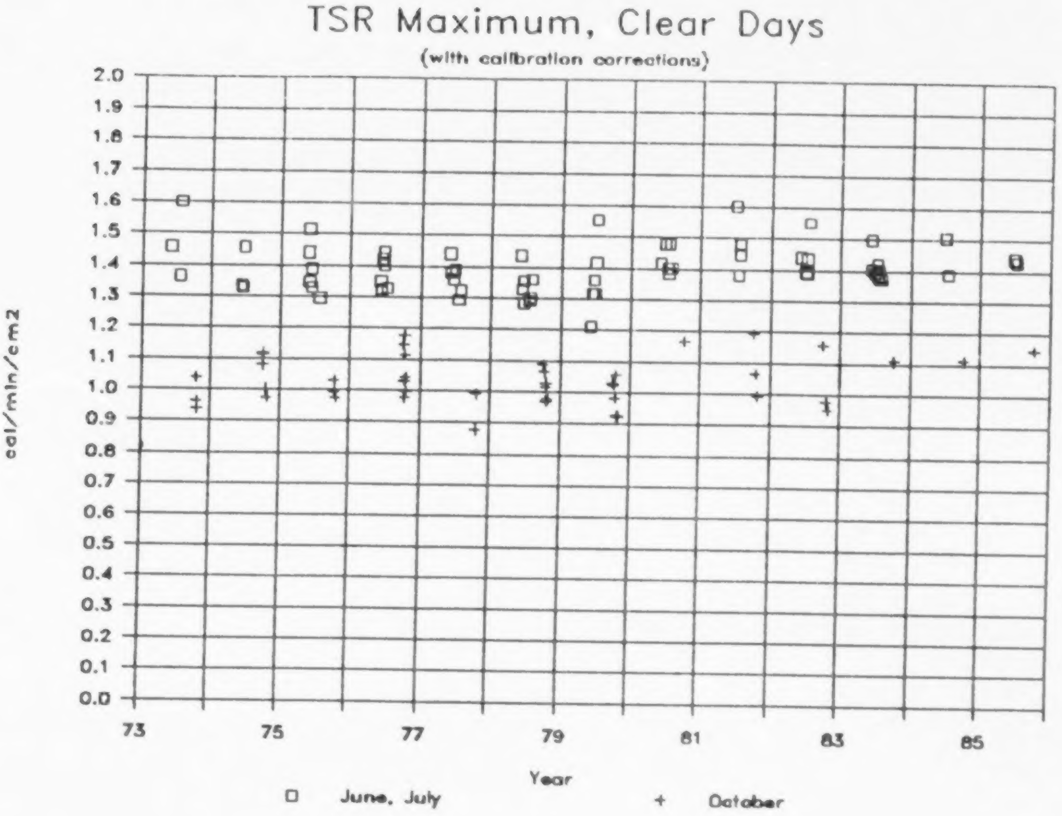


Figure E9. TSR Solar Noon Maxima (with Corrections)

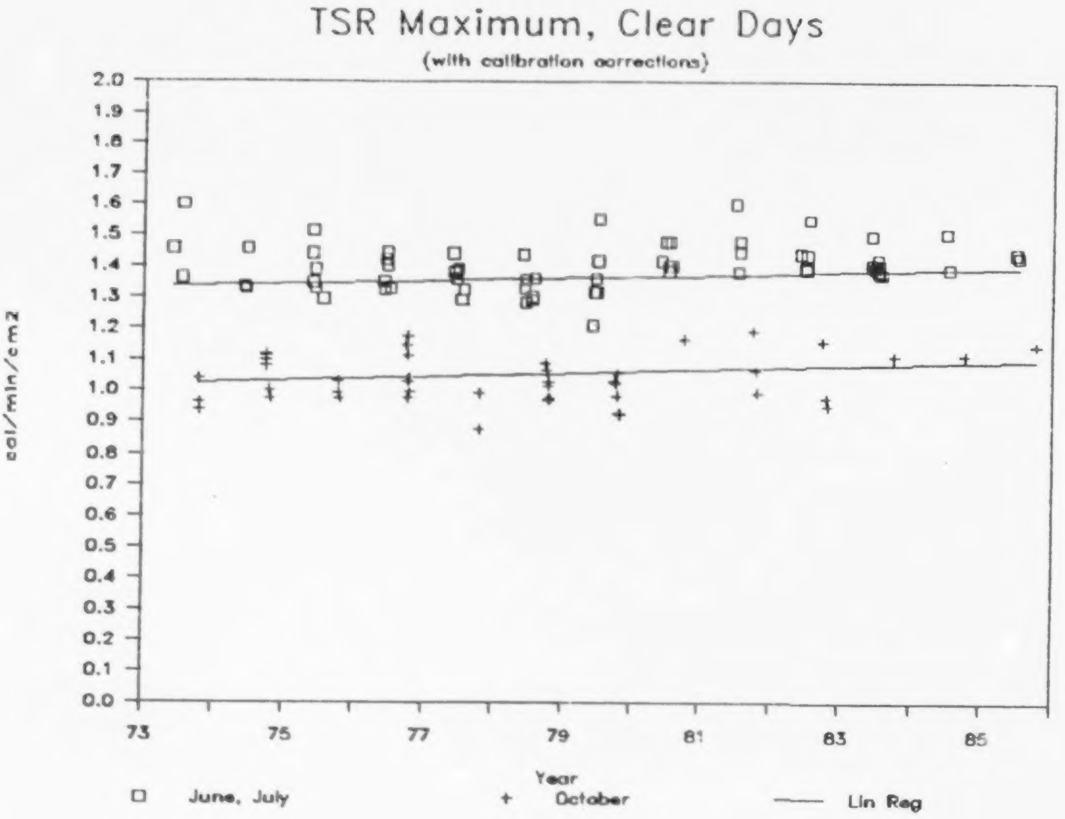


Figure E10. TSR Solar Noon Maxima (with Corrections) with Linear Regression

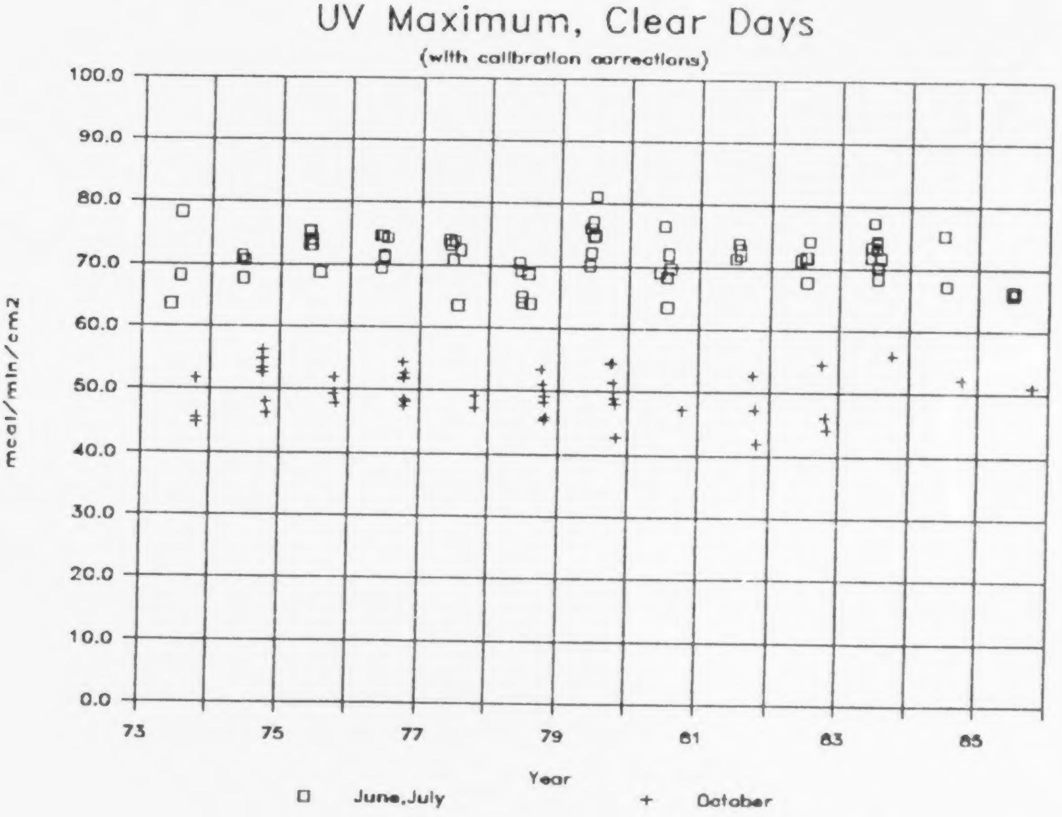


Figure E11. UV Solar Noon Maxima (with Corrections)

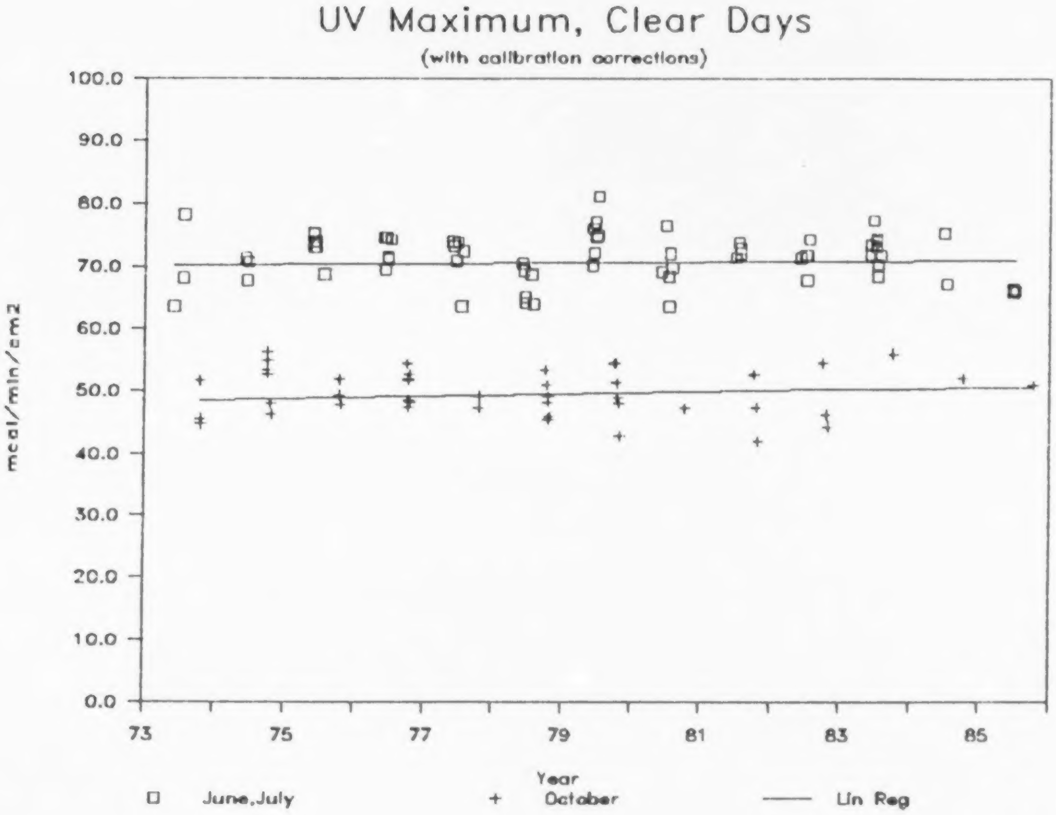


**Figure E12.** UV Solar Noon Maxima (with Corrections) with Linear Regression

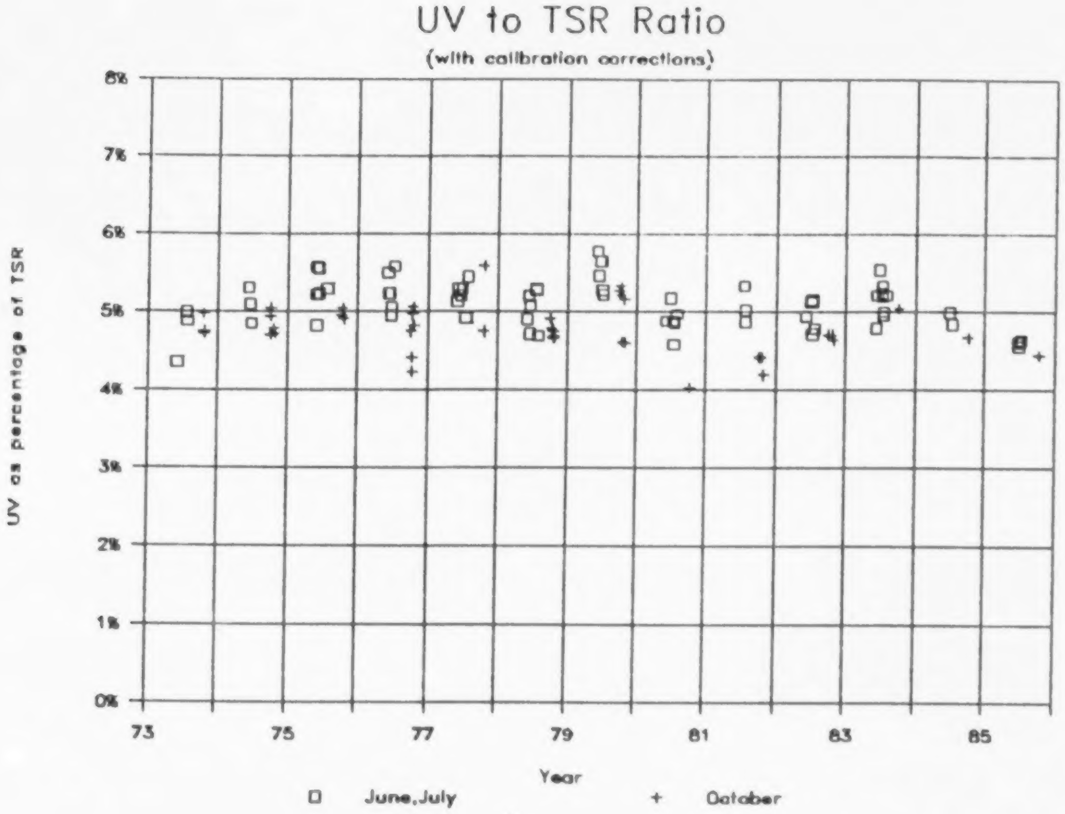


**Figure E13.** UV to TSR Ratio at Solar Noon

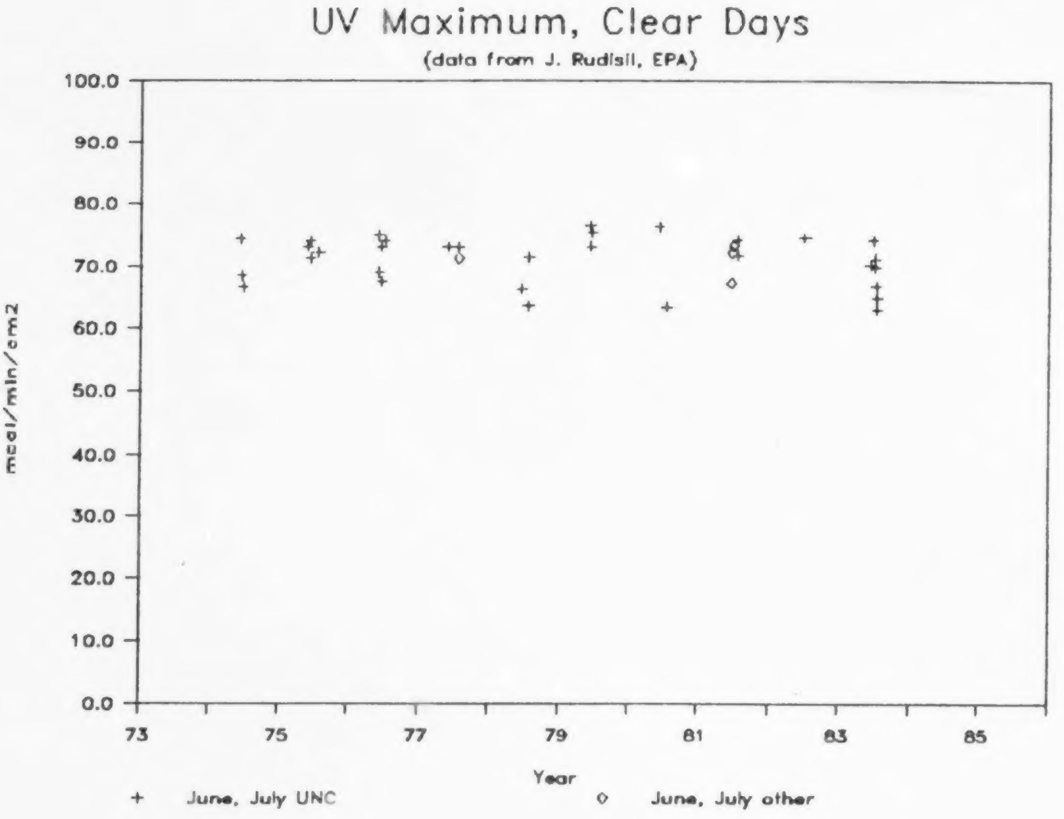


**Figure E14.** Solar Maxima from Rudisill's Data

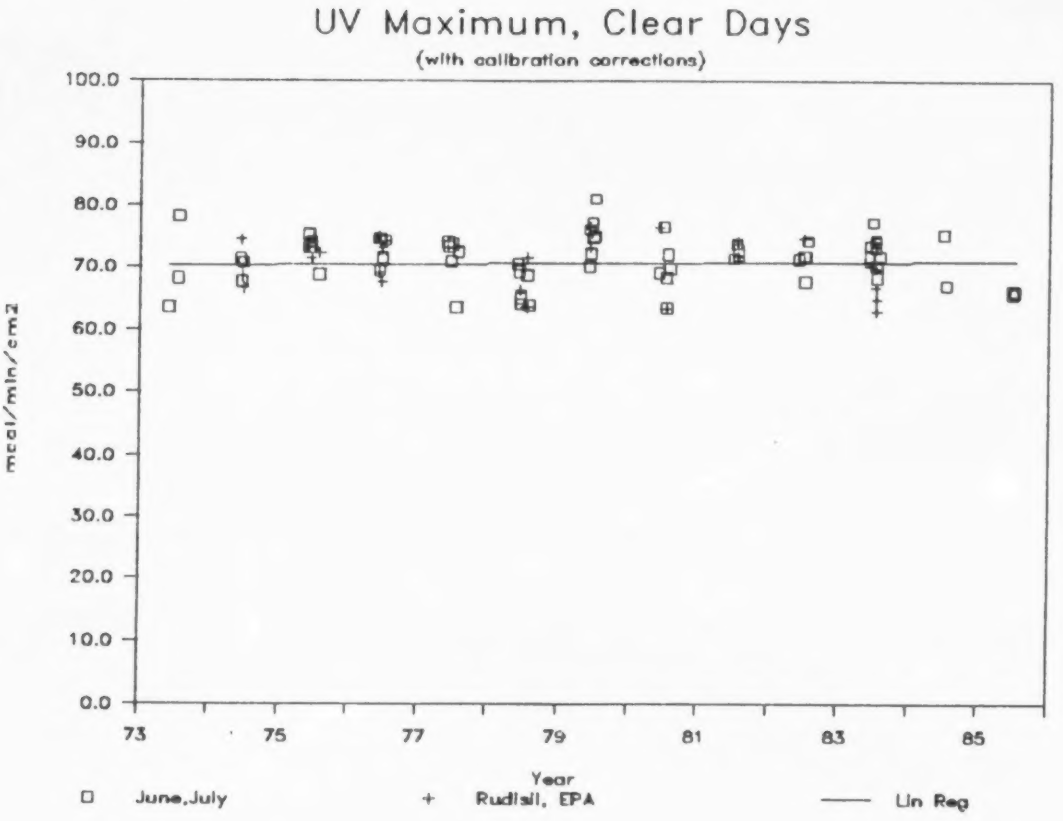


Figure E15. Solar Maxima from Rudisill's and UNC's Data

# References

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2 J. Rudisill, Division of Meteorology, Environmental Protection Agency, Research Triangle Park, North Carolina, personal communication.

3 Hatfield, J.L., J.J. Carroll, R.G. Flocchini, P.J. Smietana Jr., R.H. Hamilton, R.L. Kennedy, "Tables of Monthly Solar Radiation and Meteorological Data for Davis, California - 1979, - 1980", DOE Grant DE-FGO3-79ET20187 May 1981, Dept. of Land, Air and Water Resources Papers 10001, 10003, University of California - Davis.

4 C.G. Justus, Georgia Technical Institute, personal communication.

5 Almanac for Computer 1984, Nautical Almanac Office, United States Naval Observatory, Washington D.C. 20390

F

# Chamber and Facility

## Chamber Description

### Location

The site is approximately 32 kilometers from the University of North Carolina at Chapel Hill. It is in Chatham County, North Carolina and is approximately 10 kilometers from the small town of Pittsboro. Chatham County is one of the most rural, least industralized counties in North Carolina and is heavily wooded. The background concentrations of $NO_x$ and nonmethane hydrocarbons are usually less than 5 ppb and less than 80 ppbC. More importantly, the air exhibits very low reactivity in the chamber.

### Materials

The chamber surfaces are FEP Teflon. The film's transmission in the UV and visible regions of the solar spectrum is excellent, and it has only a few absorption bands in the IR, a property necessary to reduce the "greenhouse effect". It has a very low permeability for most chemical species and can be heat-sealed to form large durable panels. For this application its worst property is its ability to hold a static charge for long periods of time. Type A film, 0.13 mm thick is used.

### Physical Design

Inlet and outlet doors, stirring fans, manifolds and other fittings come in through a solid floor. The sides are free for light entry. The floor of the chamber is elevated approximately 1.2 m to allow for easy access under the chamber.

The design is an A-frame 9.14 m wide, 12.10 m long and 6.10 m high at the peak on a plywood floor 1.22 m above the ground. Wooden beams, 5.08 cm by 20.32 cm, located on edge at 99.1 cm centers form an exterior framework on top of the plywood floor. Continuous 16.46 m lengths of film are attached to the inside by aluminum u-channels, screwed firmly to the wooden beams, thus compressing the film against the external support. See Figure 1 and Figure 2.

One piece, heat sealed Teflon film panels are used in such places as the triangular end panels and floors. The floor-to-side seals are achieved by a 0.61 m overlap of

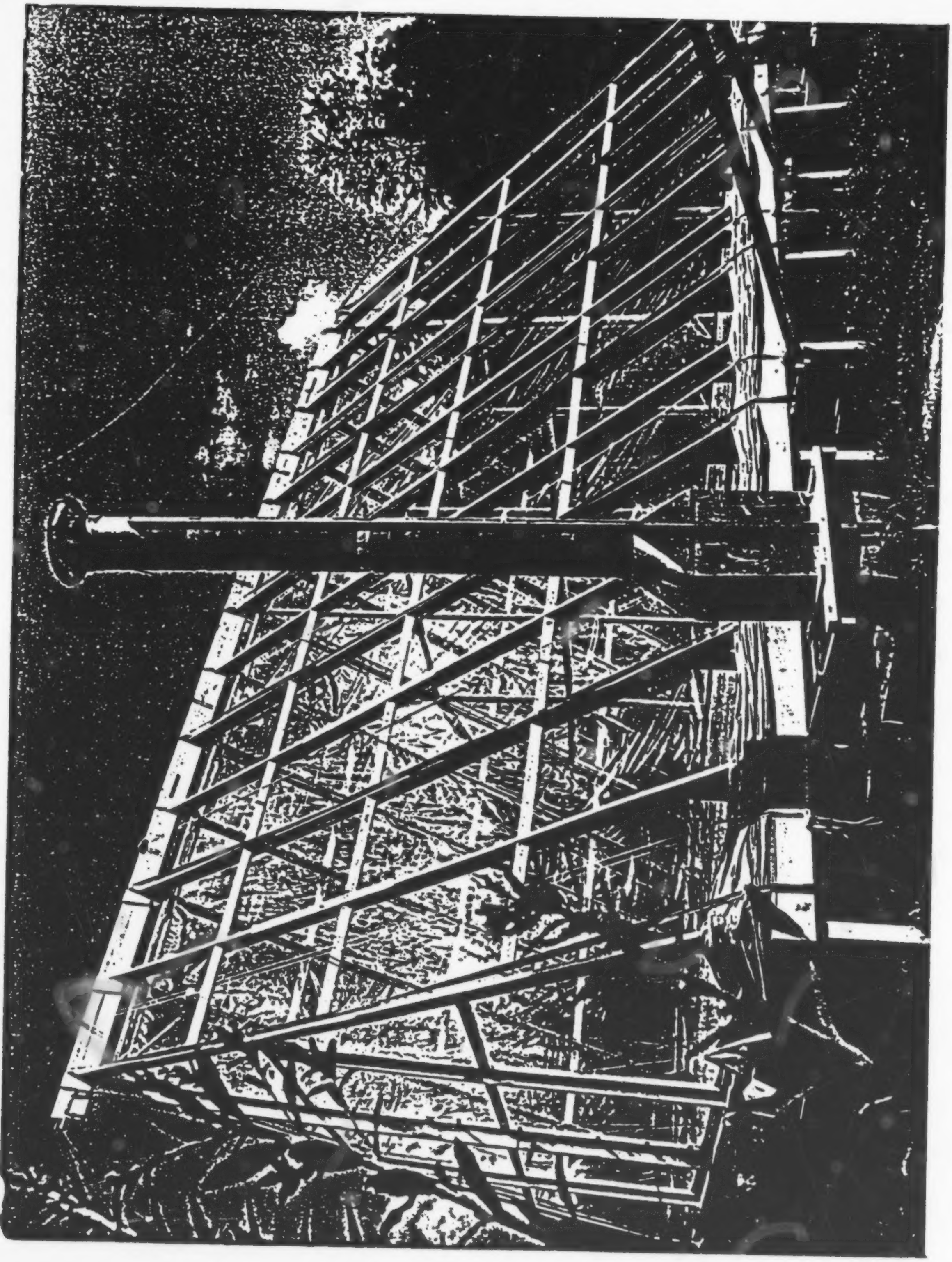


Figure 1. The University of North Carolina Smog Chamber. (Courtesy of the Greensboro Daily News)

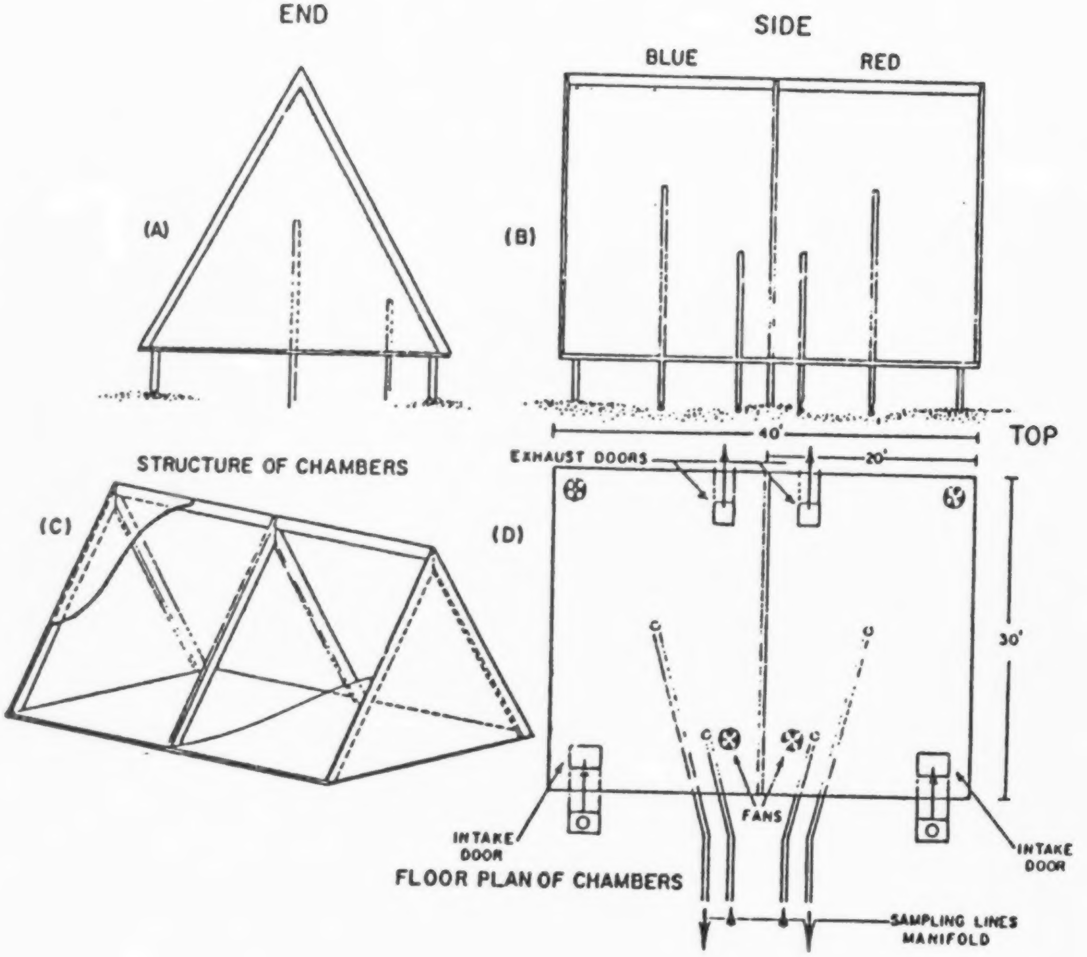

END
(A)
SIDE
BLUE
RED
(B)
STRUCTURE OF CHAMBERS
(C)
40'
TOP
EXHAUST DOORS
20'
(D)
30'
FANS
INTAKE DOOR
INTAKE DOOR
FLOOR PLAN OF CHAMBERS
SAMPLING LINES MANIFOLD

**Figure 2**. Schematic of UNC Outdoor Smog Chamber.

side panel film over floor panel film. A rubber strip under the film and an aluminum strip over top of the film complete the seal. All other seals are Teflon-to-Teflon under pressure of the aluminum u channel. A single unsupported heat sealed Teflon panel similar to the end panels is used to separate the chamber into two halves of equal volume. It is sealed to the floor and side panels in the same manner as described above. Aluminum foil is placed under the film on the floor to reflect the light and heat back up through the chamber. This is necessary to reduce solar heating of the air to a value that is within normal urban environments and to compensate for transmission losses through the Teflon film.

## Orientation

The chamber is oriented with its long axis approximately north to south. The actual long axis orientation is along a 27 -207 true heading. The orientation with respect to the sunrise and sunset at different times of the year and the altitude of the sun at noon for different times of the year are illustrated in Figure 3 and Figure 4.

## Air Handling System

There are four air handling systems in each half of the chamber, one for exhausting, one for sampling, one for recirculating through dehumidifiers, and one for mixing. The exhaust system consists of two intake stacks, 0.61 m × 0.91 m intake doors, 0.61 m × 0.61 m exhaust doors, and an exhaust blower. The exhaust blower is a dual blower on a single shaft driven by a 1.5 horsepower motor. Air enters the system through the two 5.49 m high by 30.5 cm diameter stacks. This system is designed to permit rapid exhausting of chamber contents and replacement with ambient air. The filling rate is 7190 l/min. The chamber can be flushed with a 99.6% decay of initial contents in 2 hours.

The second air handling or manifold system is for sampling and injection of pollutant materials into the chamber halves. To insure representative sampling, a 3.17 cm I.D. glass manifold runs from a point 1.83 m above the floor in the center of each chamber half down through the floor and over to a sampling laboratory. The sampling volume required by all the instruments does not exceed 5 lpm but to reduce losses due to long resident times it is necessary to have high flows in the manifold. The flow rate in the manifold is 60 lpm. The manifold system is wrapped with a controlled heating tape to maintain the sample slightly warmer than the chamber temperature. To avoid the necessity of makeup air, the sampling manifold is a closed loop. Squirrel cage blowers with housings and fans that are Teflon coated are used to circulate air through the manifolds. The unused sampler air is then returned through a 3.17 cm I.D. glass manifold to the chamber. These

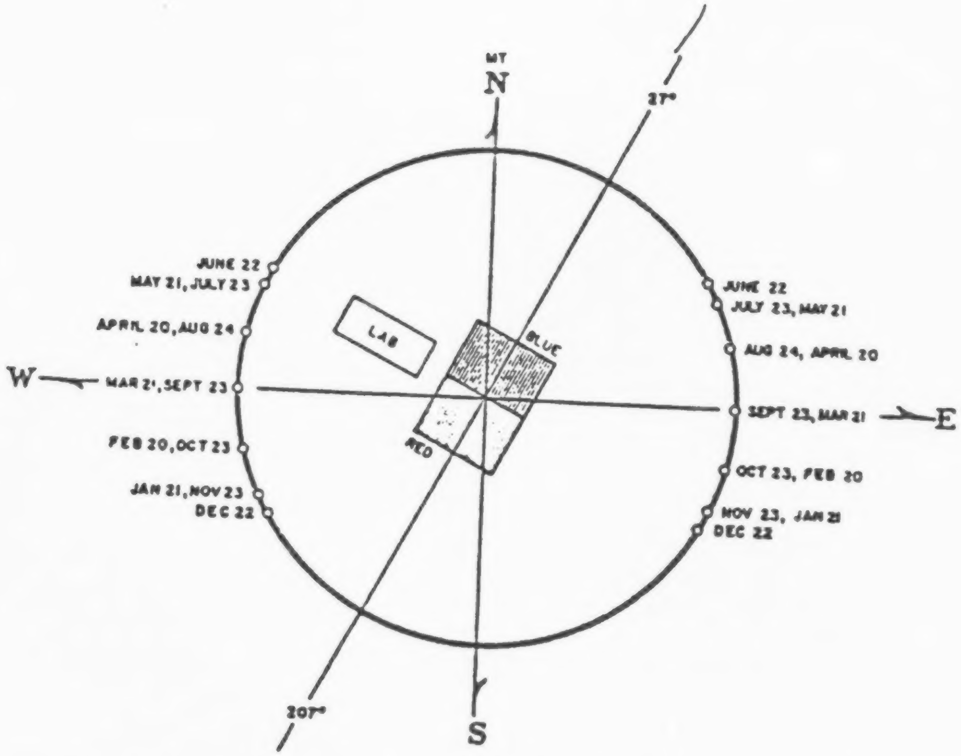

MT
N
27°
JUNE 22
MAY 21, JULY 23
APRIL 20, AUG 24
W
MAR 21, SEPT 23
FEB 20, OCT 23
JAN 21, NOV 23
DEC 22
LAB
BLUE
RED
JUNE 22
JULY 23, MAY 21
AUG 24, APRIL 20
SEPT 23, MAR 21
E
OCT 23, FEB 20
NOV 23, JAN 21
DEC 22
207°
S

**Figure 3.** Orientation of UNC Outdoor Smog Chamber with respect to seasonal sunrise and sunset positions.

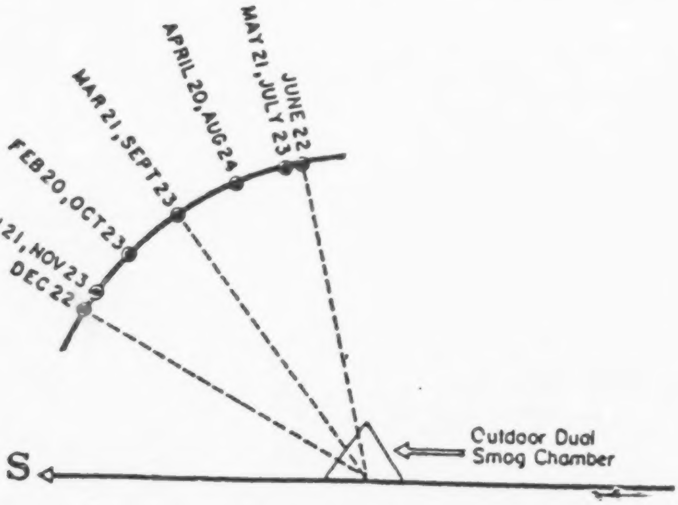

JUNE 22
MAY 21, JULY 23
APRIL 20, AUG 24
MAR 21, SEPT 23
FEB 20, OCT 23
JAN 21, NOV 23
DEC 22
Outdoor Dual Smog Chamber
S

**Figure 4.** Solar altitude and zenith angle at noon at the UNC Outdoor Smog Chamber for each month.

return manifolds provide a convenient method for injecting the initial reactants. There is also a special heated Teflon manifold for formaldehyde sampling.

Inside each chamber half are two mixing fans located in opposite corners. These provide circulation and mixing of the chamber contents. The fans are 50.8 cm diameter cast aluminum units that are FEP Teflon coated. They operate in a horizontal position, 0.76 m above the floor on 2.54 cm diameter Teflon coated steel shafts that extend through the chamber floor. Under the floor, 1/4 horsepower, 1750 rpm motors provide power through a belt and pulley system to each fan. Each fan operates at approximately 31.15 $m^3$/min.

## Laboratory

The laboratory is adjacent to the chamber. It is a 3.66 m W × 15.24 m L × 3.05 m H temperature-controlled wooden structure oriented perpendicular to the chamber and 3.66 m away from it to avoid any shadowing.

The first 5.49 m nearest the chamber contain the instrumentation, manifolds, and calibration systems. At the sample inlet of each gas instrument is a three way Teflon AC solenoid valve. Since there are two intake manifolds (one for each chamber half), air from either manifold can be drawn through the three-way valve and into the instrument. In this manner timesharing of one instrument between the two chamber halves is possible.

The next 5.49 m contain the data acquisition computer system (described in the Data Acquisition System section) and the operations area. The last 4.27 m of the laboratory is a utility area with running water and storage facilities.

Gas tanks necessary to operate the instruments and perform calibration are located in a 1.22 m × 1.83 m room completely closed off from, but attached to, the laboratory. The injection system gas tanks and valves are housed in a second 1.52 m × 1.52 m well-insulated heated room adjacent to the end of the laboratory nearest the chamber.

## Injection System

Pollutants are injected into the chamber sides via the return side of the sampling manifolds. The return manifolds enter the chamber sides under one of the mixing fans. The injection process uses gas cylinders containing pollutants at high concentration (1000-10,000 ppm range), two-stage stainless steel diaphragm regulators, on-off solenoid valves, and a precision needle valve. The flow rate of injected material into the manifolds is established by a mass flow meter with a 5 millisecond response time. The total injection volume is accurately controlled as a function of the time the solenoid valve is open. The open time of each solenoid valve is controlled by the computer system on command. Conditions can be varied sufficiently to have the injection time range from a few seconds for each component to 1-2 hours for a programmed injection used to simulate the buildup of pollutants in urban areas.

G

# Analytical Methods

## Introduction

The analytical instrumentation in the gas laboratory adjacent to the large outdoor chamber at UNC includes: eight packed column or capillary gas chromatographs for hydrocarbon, organic nitrate, and inert tracer analysis; one liquid chromatograph for DNPH-aldehyde analysis; an automated wet chemical formaldehyde instrument, two ozone and $NO_x$ chemiluminescent monitors; and one UV ozone photometer. The laboratory also contains all of the associated calibration systems used for these instruments. In addition, solar and UV radiation sensors are mounted on top of a 7 meter tower next to the laboratory. Chamber temperature measurements are made with an inline thermistor located in the inlet of each chamber sampling manifold. The manufacture and calibration methods for all of these systems are listed in Table 1 and Table 2.

## Hydrocarbons

Total hydrocarbons (THC), methane ($CH_4$) and CO are analyzed with a Beckman 6800 gas chromatograph. Figure 1 shows a typical Beckman 6800 measurement cycle. This cycle occurs every 5 minutes and each side of the chamber is sampled for 30 minutes. Unfortunately, methane responds differently than non-methane HC on this type instrument requiring a separate methane calibration as well as a NMHC calibration.

A manually operated valve on a Carle 211 gas chromatograph (designated Carle 1) is also used to obtain total non-methane hydrocarbon data. This system introduces a sample directly into a blank column and then to the FID. Figure 2 shows how this instrument is used to match the THC injected in the two chamber halves. The increase in the chamber THC is clearly shown as well as the degree of relative matching of the two chamber sides. This THC method is used primarily in the morning during injection and the regular operation of the Carle 1 is used for the rest of the run.

Three automated Carle Model 211 packed column FID gas chromatographs are used for $C_1$-$C_{10}$ analysis. The first of these chromatographs, Carle 1, is used to perform a gross analysis on $C_2$-$C_{10}$ hydrocarbons. Three chromatographic columns

Table 1. Analytical Methods, Characteristics, and Operation Methods

| Substance | Method | Manufact and Model | MDC | Range | Mode | Time Shared |
|---|---|---|---|---|---|---|
| $O_3$ | Chemiluminescence | Bendix 8002 | 0.001 | 0-2 | Continuous | Yes |
| NO, $NO_x$, $NO_2$ | Chemiluminescence | Bendix 8101-B | 0.005 | 0-1 | Cyclic, 4 min | Yes |
| HC's alkenes,alkanes, aromatics | Automated multiple column GC-FID | Carle 211 | 0.005-0.010 | 0-100 | Cyclic, 15 min | Yes |
| THC, CO, $CH_4$ | Automated multiple column GC-FID | Beckman 6800 | 0.010 | 0-80 | Cyclic, 15 min | Yes |
| HCHO | Automated Colorimetic(reverse West-Gaeke) | CEA 555 | 0.01 | 0-2 | Continuous | Yes |
| Acetaldehyde, propionaldehyde, MEK | Automated multiple column GC-FID | Carle 211M | 0.02-0.05 | 0-100 | Cyclic, 30 min | Yes |
| Aromatics HC, aromatic aldehydes, phenols | GC-FID | Perkin-Elmer 900 | 0.010 | 0-100 | Manual | Yes |
| Halocarbon tracers | GC-EC variable freq. pulsed bais detecter | Analog Tech. Corp. | 0.0004 | 0-1 | Cyclic, 30 min | Yes |
| PAN and Alkyl nitrate | GC-EC DC based EC Model 940 | Varian Aerograph | 0.0003-0.0005 | 0-1 | Cyclic, 30 min | Yes |
| $HNO_3$ | Chemiluminescence, molybdenum converter, nylon scrubber | Bendix 8101-B | 0.003 | 0-1 | Cyclic, 15 min | No |
| $H_2O_2$ | sample taken manually with bubbler; analysis using automated chemilum. method | | 0.0001 | 0-1 | Manual . | Yes |
| Temperature | Thermistor | YSI | 0.2°F | 20-110°F | Continuous | No |
| TSR | Pyranometer | Eppley Black and White | 0.001 Langly | 0-2 Langly | Continuous | No |
| UV | Pyranometer | Eppley UV | 0.1 mLangly | 0-100 mLangly | Continuous | No |
| Dew Point | Cooled mirror | EGandG 880 | 0.1°F | -40 to 120°F | Continuous | Yes |

Table 2 . Calibration Sources for Gases

| Species | Source | Calibration Method | References |
|---|---|---|---|
| $O_3$ | UV-quartz $O_3$ generator | UV photometry Dasibi Model 1008-AH | EPA |
| NO | Cylinder $O_3$ UV photometry | Certified commercial analysis and transfer via Gas Phase titration | EPA |
| $NO_2$ | Oxidaton of NO | Gas Phase Titration | EPA |
| $CH_4$, CO, THC | Cylinder | Certified commercial analysis | EPA |
| HC's | Cylinder | Certified commercial analysis | EPA |
| HCHO | paraformaldehyde and 37% HCHO | Prepared static calibration standards verified with chromotropic acid bubbler technique | |
| Acetaldehyde, propionaldehyde, MEK | pure compounds | Prepared static calibration standards | |
| Aromatics | pure compounds | Prepared static calibration standards | |
| PAN | PAN purified | Reference method and transfer standard | Winer, A. *et al.* EST 8 p1116, (1974) |
| Alkyl nitrates | pure alkyl nitrates | Prepared static calibration standards | |
| $HNO_3$ | $HNO_3$ (gaseous) | Dynamic source (gas) calibrated by colorimetric (chromotropic acid) bubbler method | Spicer, C., Adv. Envr. Sci. and Tech. 7 p163 (1980) |
| H2O2 | liquid H2O2 | Liquid standards and iodometric analysis | |

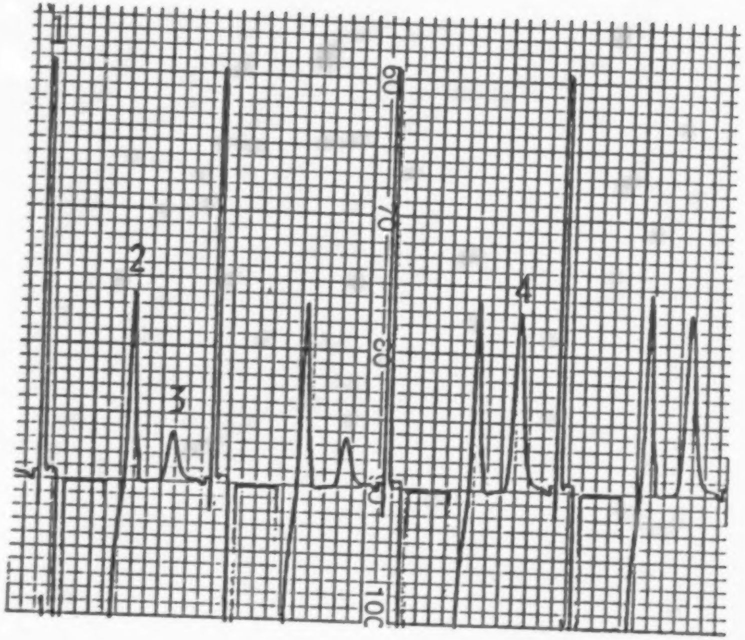


**Figure 1.** Example Chromatograms from Beckman 6800 Gas Chromatograph. Peaks: (1) Total Hydrocarbons — 4.0 ppmC, Attenuation × 2; (2) Methane — 2.5 ppmC, Attenuation × 1; (3) CO — 9.9 ppmC, Attenuation × 2; (4) CO — 37.2 ppmC, Attenuation × 2.

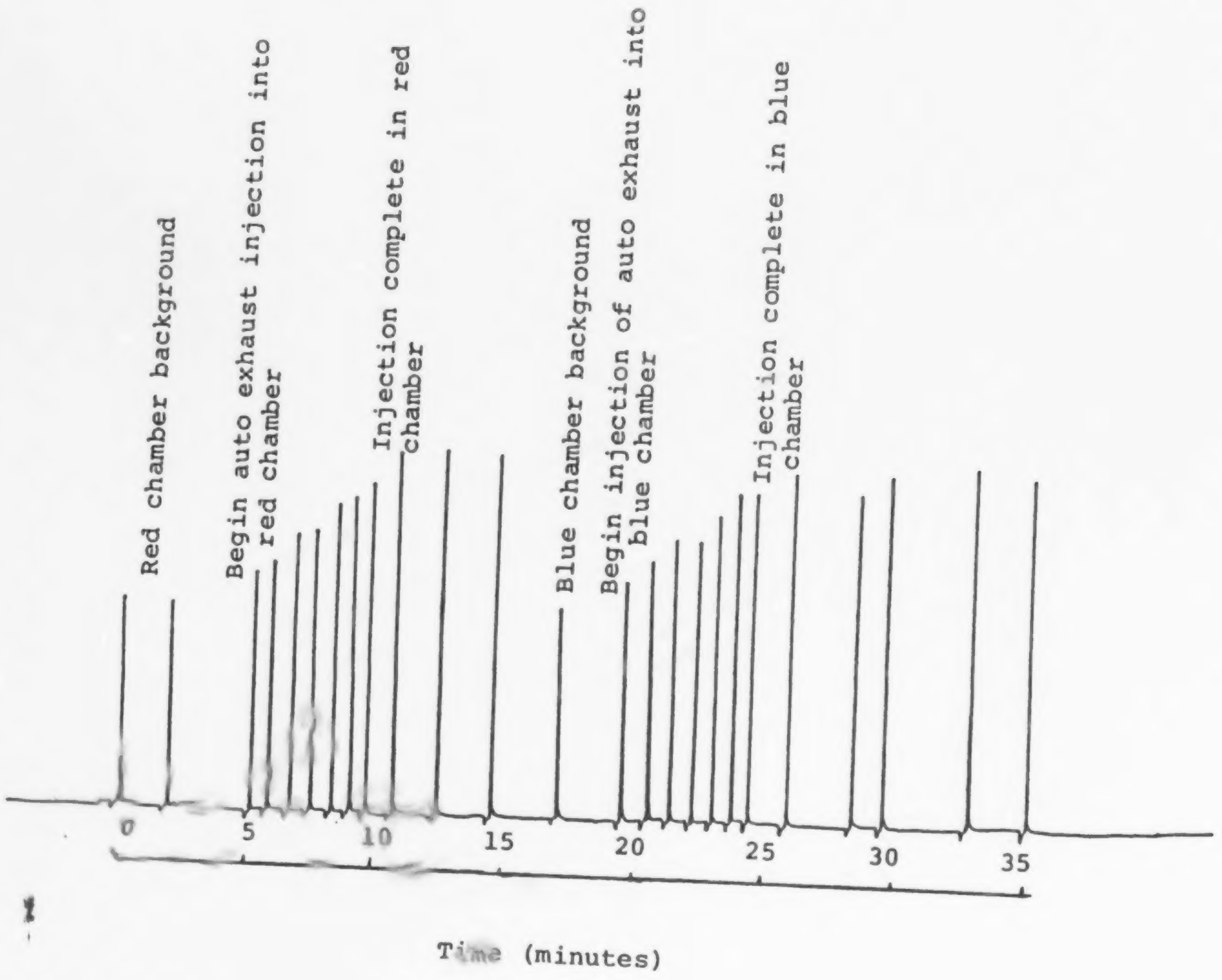


**Figure 2.** Monitoring of total hydrocarbon concentration as auto exhaust is injected into UNC Outdoor Chambers with a 10 cc direct injection into the flame detector of a Carle I model 211 gas chromatograph.

perform the analytical separation. An additional 2' × 1/8" column of carbowax 400 was installed just before the flame detector to balance column bleed and prevent excess baseline displacement after valve switches.

The columns used in Carle 1 are:

Column 1

6' × 1/8" carbowax 1540 + 5% Apeizon L on Supelcoport 80/100 mesh support to separate $C_6$-$C_8$ paraffins, olefins and aromatics

Column 2

6' × 1/8" N-octane/Poracil C 100/120 mesh (baked at 240°C for 2 hrs.) + 2' × 1/8" 20% Apeizon L on Supelcoport 80/100 mesh to separate $C_4$ and $C_5$ olefins and some $C_6$ paraffins

Column 3

2' × 1/8" FL alumina treated with 5% NaCl to separate $C_1$-$C_3$ compounds.

Motor activated 6 port valves shunt the sample to the appropriate columns. The valves are controlled by a 30 minute 110 volt Carle programmable timer. The column configurations for each valve position are shown in Figure 3. The indicated restrictors are adjustable S.S. 1/16" Nupro needle valves and are used to match the pressure drop across various columns as these columns are switched in and out of the flow circuit.

Automatic injection is made with all three columns in series. One and one half minutes are required for the individual compounds to become distributed into the proper columns. Since column 1 is the first to be encountered, $C_6$-$C_8$ are retained, while $C_1$-$C_5$ pass on to column 2. After this first 1.5 minutes with the columns in series, a valve switch removes column 2 and 3 from the flow path and permits the compounds in column 1 to elute into the FID. The system remains in this configuration for 5.5 minutes so that $C_6$-$C_{10}$ paraffins and toluene can be eluted. We also extend this time to 14 minutes to measure xylenes or $\alpha$-pinene.

A second valve switch then briefly (1 minute) places columns 1, 2, and 3 back in series so that methane and ethylene can be detected. During this period, propane and propylene move from column 2 to column 3 but do not elute before the third valve switch. This switch removes column 3 and leaves columns 1 and 2 in series with the detector. Butenes, pentanes and pentenes then elute from column 2. Finally, with only 2.5 minutes remaining in the cycle, the columns are placed back in series so that propane, propylene and acetylene can be measured.

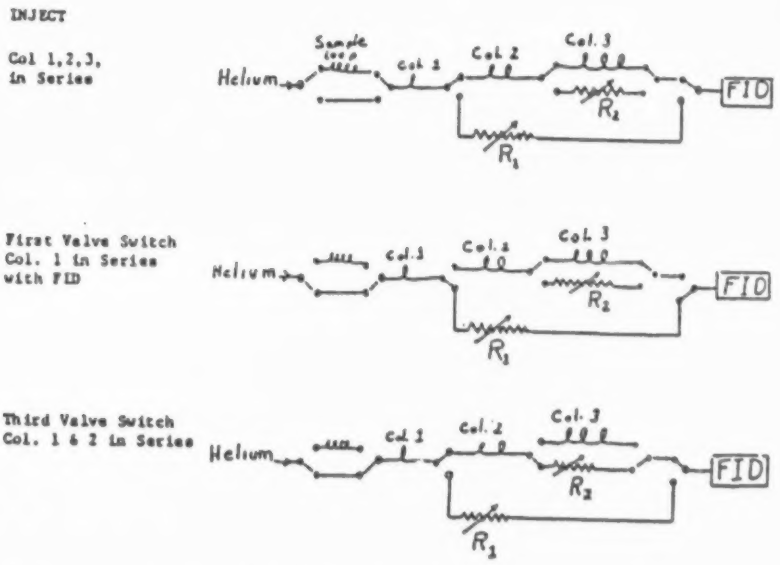

INJECT
Col 1,2,3, in Series
Sample loop
Helium
Col 1
Col 2
Col. 3
FID
$R_2$
$R_1$
First Valve Switch Col. 1 in Series with FID
Helium
Col. 1
Col. 2
Col. 3
FID
$R_2$
$R_1$
Third Valve Switch Col. 1 & 2 in Series
Helium
Col 1
Col. 2
Col. 3
FID
$R_2$
$R_1$

Figure 3. Column and Valve Configuration for $C_1$-$C_{10}$ Automatic Carle Chromatograph.

A chromatogram of the UNC mix is shown in Figure 4. The operating sensitivity can be as low as 7 to 15 ppbC (at a signal to noise ratio of 2 on the most sensitive scale). A limitation of this system is that ethylene and ethane, acetylene and propylene, and some $C_4$ and $C_6$ compounds are not completely resolved.

A second packed column GC (Carle II) is used to measure $C_1$-$C_3$ hydrocarbons and selected carbonyl species. It employs a 2 m × 1/8" ss, 60/80 mesh porapack Q column for $C_1$-$C_3$ separation and a 3 m 1/8" SS 10% carbowax 20M (80:100 supelcoport) column for the carbonyls; toluene and xylenes also elute from this column. As with Carle I, Carle II uses motor activated valves and a programmable valve controller. A 5-cc air sample is injected onto each column every 15 minutes. While one column is in series with the flame detector, the other is being back flushed. A typical 30 minute analysis on this system is shown in Figure 5.

The third packed column chromatograph (Carle III) is used to resolve $C_4$ and $C_5$ hydrocarbons on one column and aromatics on the other. It uses a GP 80/100 mesh, Carbopack 19% picric acid, 1/8" SS × 3 m column for $C_4$ and $C_5$ and 1/8" × 3 m, GP 10% TCEP, on 100-120 Chromosorb AW column for aromatics. A valve diagram of this system and a chromatographic analysis of auto exhaust are shown

CONCENTRATIONS OF INDIVIDUAL SPECIES IN
0.39 PPMC NMHC UNC MIX

| | COMPOUND | CONCENTRATION (PPMC) |
|---|---|---|
| 1 | 2-METHYLPENTENE | 0.035 |
| 2 | 2,4-DIMETHYLPENTENE | 0.039 |
| 3 | 2,2,4-TRIMETHYLPENTANE | 0.040 |
| 4 | ETHYLENE | 0.042 |
| 5 | BUTENE-1 | 0.010 |
| 6 | BUTENE-2 | 0.013 |
| 7 | ISOPENTANE | 0.053 |
| 8 | N-PENTANE | 0.092 |
| 9 | 2-METHYLBUTENE-1 | 0.008 |
| 10 | 2-METHYLBUTENE-2 | 0.007 |
| 11 | PROPYLENE/ACETYLENE | 0.047 |

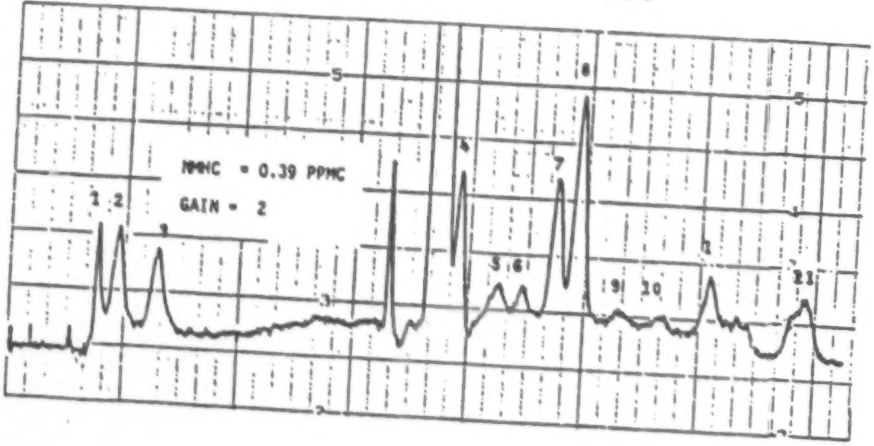


Figure 4. Maximum sensitivity of Carle chromatograph on attenuation of X1 and gain of 2.

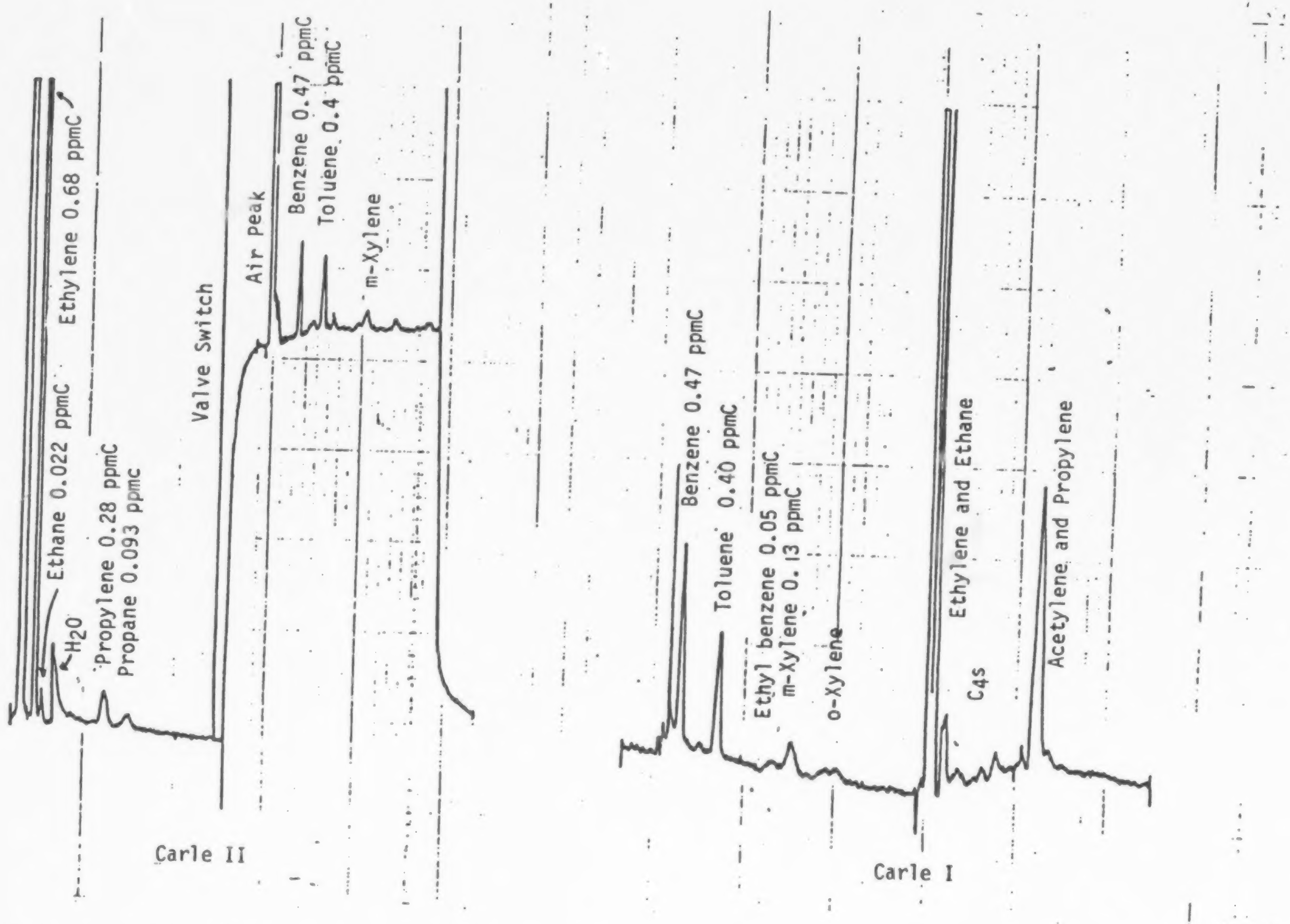


**Figure 5** . Analysis of $C_1$-$C_8$ hydrocarbons in 4 ppmC dilute chamber auto exhaust on Carle II (Model 211) packed column gas chromatograph (July 1, 1982).

in Figure 6 and Figure 7.

As can be seen, many compounds such as propylene, butenes, toluene and xylenes can be detected by two or even all three of these chromatographs. Most compounds can be quantitatively determined at concentrations of 0.05-0.1 ppmC and, in instances when peaks are sharp, at levels of 0.01 ppmC. The output from each of these instruments is monitored with a Perkin Elmer Sigma 10 integrator and also with stripchart recorders. Since 30 minutes is required for one complete analysis a sample from each chamber is taken every hour.

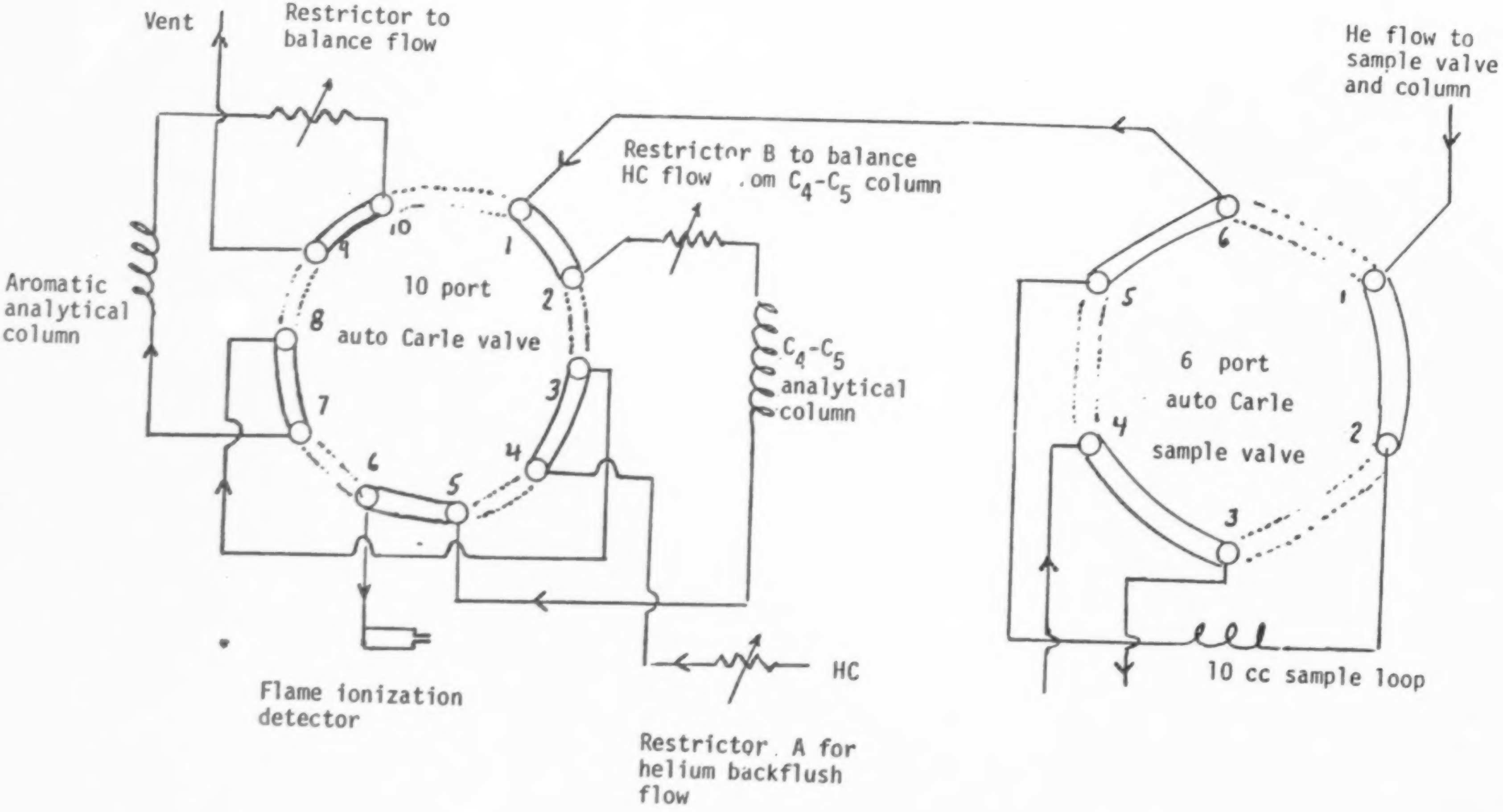
Aromatic compounds are detected with greater sensitivity and resolution by two capillary FID gas chromatographs. The first system was built around a Perkin Elmer 900 gas chromatograph and the second uses a Perkin Elmer Sigma 1.

A plumbing diagram for the first system is shown in Figure 8. Programmed signals from the Sigma 1 integrator autoactuate two 6-port, pneumatically operated valves which allow multiple 11-cc samples to be trapped in a freeze-out loop. The sample is then automatically desorbed onto a 30 m DB 1 (J & W) or SP2100 (H.P.) fused silica column.

The freeze-out loop has an internal volume of 50 to 150 μliters. It is packed with 60/80 mesh glass beads to increase the internal surface area and decrease the internal dead volume. The effective internal volume is ≈ 25-75 μliters. A dry ice/methanol bath is manually used to cool the trap. The loop is wrapped with fiberglass insulated nichrome wire for the thermal desorption and will heat the loop from liquid nitrogen temperatures to 200°C in less than one minute.

The operating cycle is controlled by a solid state controller. After an initial hold of 6 minutes for valve switching, the column is programmed from 40°C to 150°C at 6.5°C per minute.

This system will separate hydrocarbons from $C_6$ through $C_{14}$. A wider range is possible using sub-ambient column temperatures. A typical calibration chromatogram from a mixture of hydrocarbons injected into the chambers is shown in Figure 9 and an analysis of dilute chamber auto exhaust in Figure 10. Benzaldehyde, tolualdehydes, cresols, nitro benzenes, nitro and toluenes, nitro cresols and dimethyl phenols can also be monitored with this system. The analytical sensitivity of this GC to most compounds is in the 5 ppbC range. A complete analysis requires 45 minutes, including oven cooldown and injection. Thus one sample is taken from each chamber every 1.5 hours.



Vent
Restrictor to balance flow
He flow to sample valve and column
Restrictor B to balance HC flow .om $C_4$-$C_5$ column
Aromatic analytical column
10 port auto Carle valve
1
2
3
4
5
6
7
8
9
10
$C_4$-$C_5$ analytical column
6 port auto Carle sample valve
1
2
3
4
5
6
Flame ionization detector
HC
Restrictor. A for helium backflush flow
10 cc sample loop

**Figure 6.** Plumbing diagram to Carle III pack column as chromatograph for the analysis of $C_4$-$C_6$ hydrocarbons and aromatic compounds. He flow through columns – 35 cc/min, backflush He – 45 cc/min, restrictions are 1/16" SS needle valves, oven temperature 60°C.

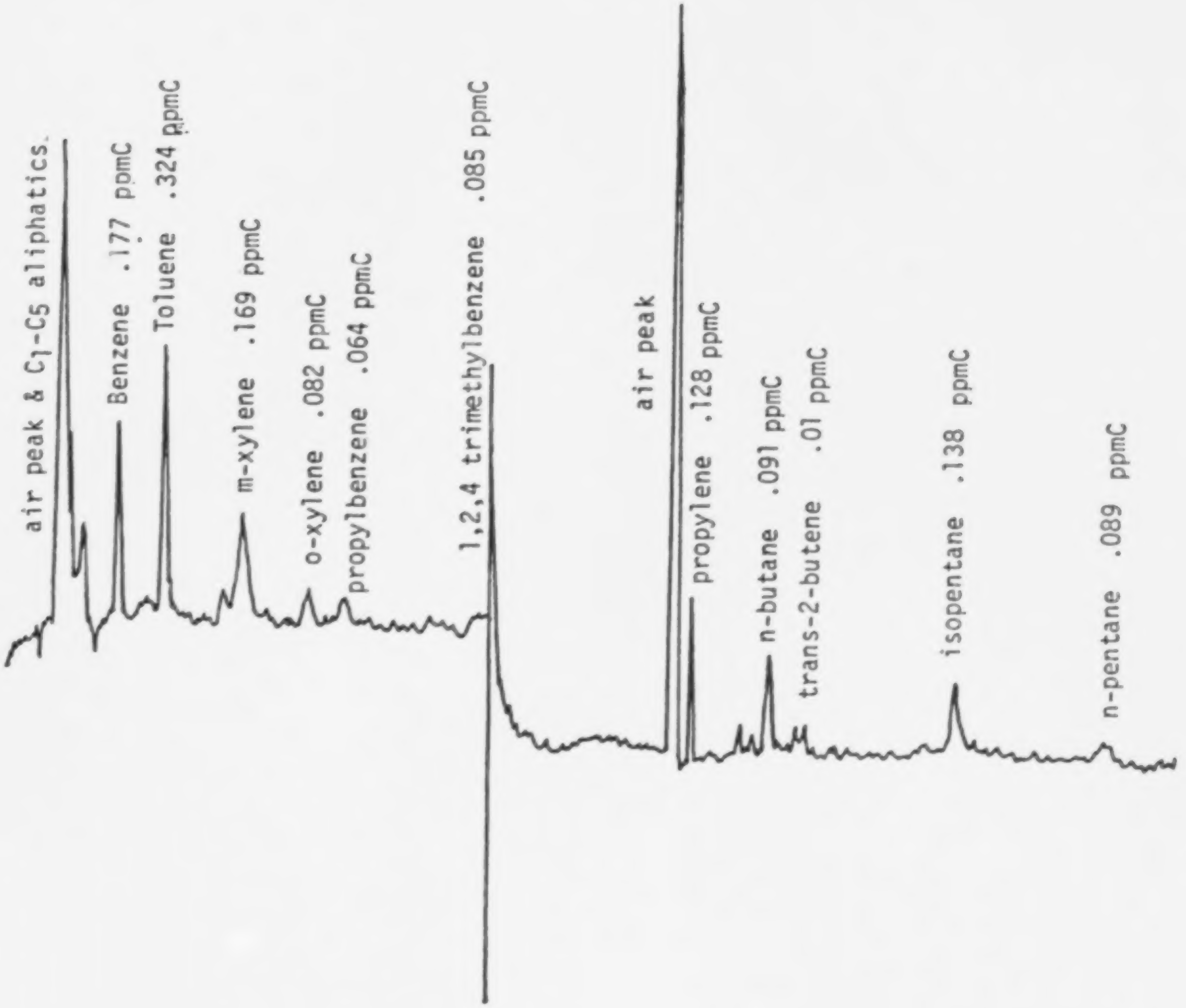


**Figure 7**. Analysis of aromatics and $C_4$-$C_5$ hydrocarbons from dilute auto exhaust injected into UNC outdoor chambers, October 4, 1983.

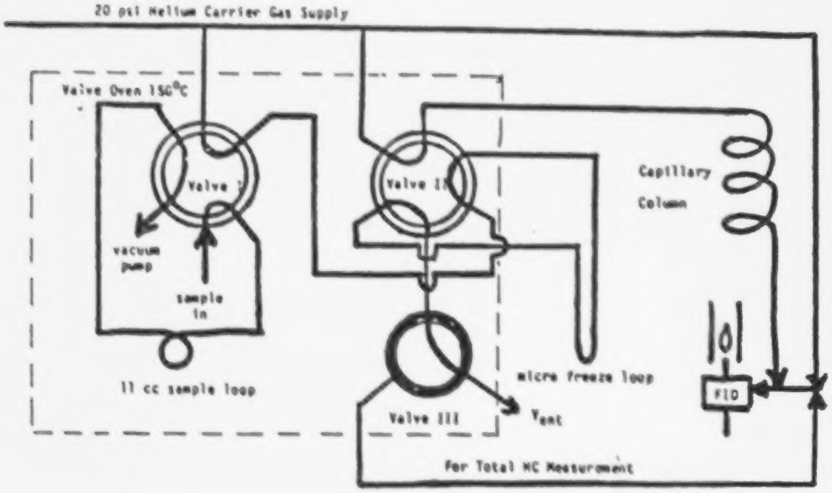

20 psi Helium Carrier Gas Supply
Valve Oven 150°C
Valve I
Valve II
vacuum pump
sample in
11 cc sample loop
Valve III
Vent
micro freeze loop
Capillary Column
FID
For Total HC Measurement

Figure 8. Plumbing Diagram for Perkin Elmer Capillary GC for Aromatic Analysis.

The fully automated capillary system was designed at UNC around a Perkin Elmer Sigma I GC and a Spectra Physics 4100 integrator. A separate controller box was built to drive a $LN_2$ cryogenic sample concentrator and then thermally degas the trapped HC species onto a 30m DB-1 capillary column. Prior to the start of an analysis the oven is cryogenically cooled with $LN_2$ to -40°C and then programmed to 180°C; one complete cycle requires 45 minutes and compounds in the $C_6$-$C_{10}$ range can be analyzed with a sensitivity of 1-3 ppbC. The advantage of this system is its increased sensitivity and the potential to ultimately monitor $C_3$-$C_{12}$ hydrocarbons in one chromatographic cycle. This permits us to analyze most hydrocarbons on one system and provide better estimates of paraffin to olefin ratios. An example chromatogram of a calibration mixture is shown in Figure 11.

## Mass Spectrometry

Individual identification of hydrocarbon species in mixtures as complex as auto exhaust is performed at UNC on a VG micro-mass 707F mass spectrometer interfaced to a Hewlett Packard 5710A capillary gas chromatograph. One to two cc of raw auto exhaust are injected onto a 30 m, SE54, or DB-1 fused silica column. The first 0.3

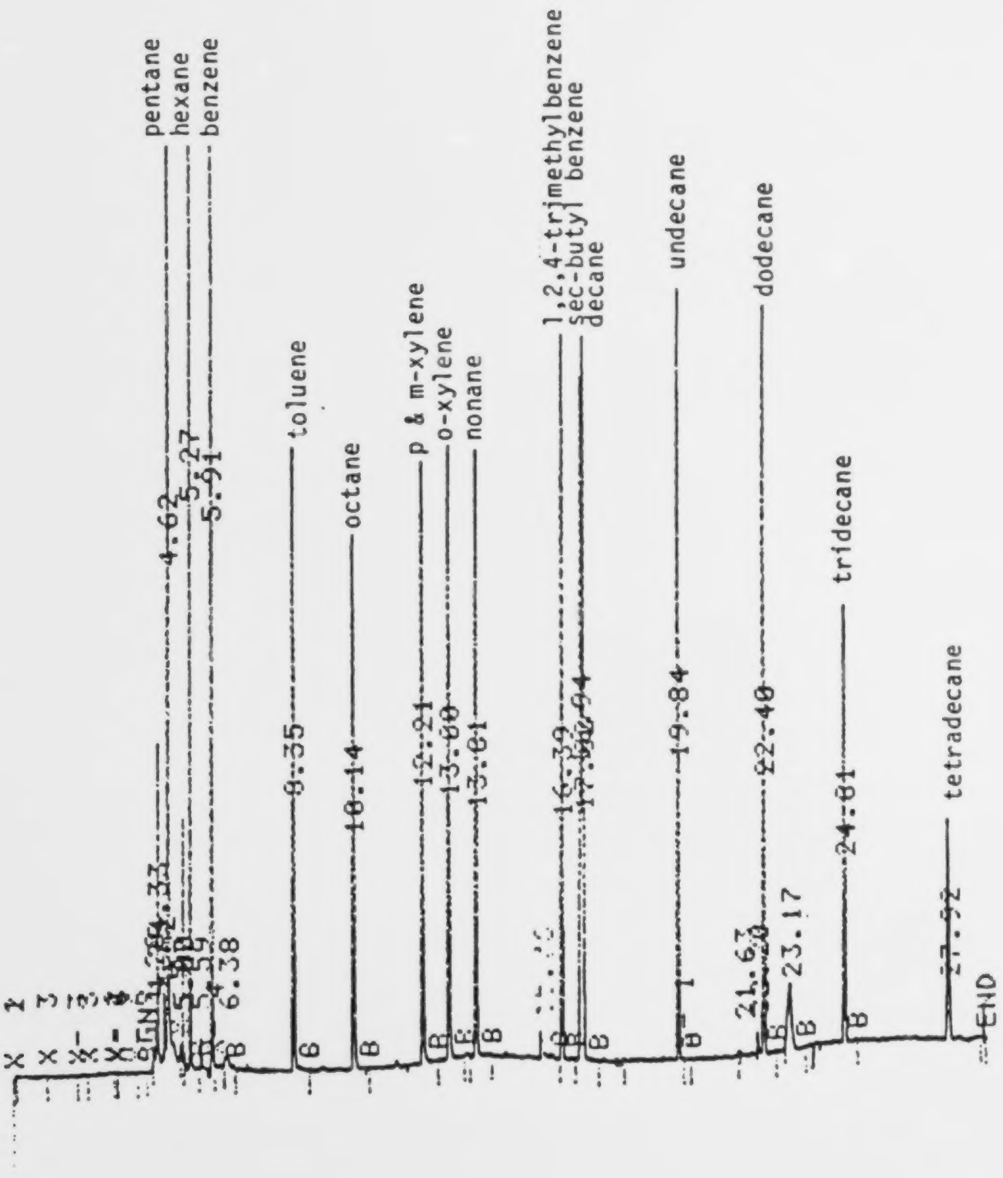


Figure 9. Calibration Chromatogram on PE 900 FID Gas Chromatograph 30 m DB-1 fused silica column (J&W), 22 cc air sample concentrated in 1/16" × 8" SS tube packed with 60/80 mesh glass beads (internal volume 25-75 ul) cooled with MeOH dry ice and thermally desorbed at 200°C with heat tape. Initial oven temperature = 40°C and programmed at 6.5°C/min to 150°C.

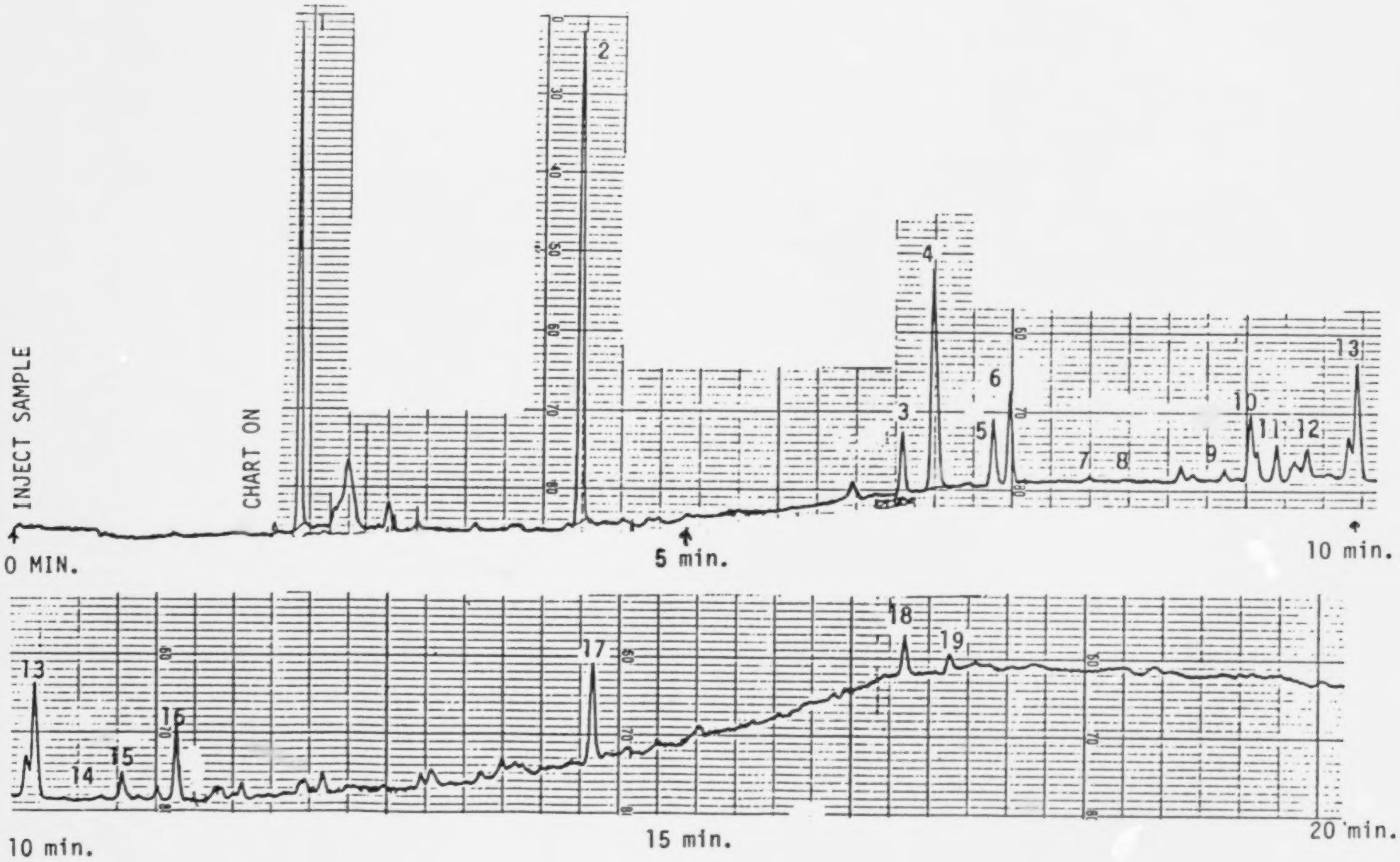


**Figure 10.** Analysis of $C_6C_{12}$ aromatics on PE 900 FID capillary gas chromatograph from a 3 ppmC dilute auto exhaust chamber run on June 30, 1982. Compound identities and concentrations are: 1) benzene, 0.337 ppmC 2) toluene, 0.366 ppmC 3) ethylbenzene, 0.051 ppmC 4) m&p-xylene, 0.187 ppmC 5) styrene, 0.059 ppmC 6) o-xylene, 0.078 ppmC 7) nonane 8) isopropylbenzene 9) n-propylbenzene, 0.012 ppmC 10) m-ethyltoluene, 0.057 ppmC 11) 1, 3,5-trimethylbenzene, 0.032 ppmC 12) o-ethyltoluene, 0.017 ppmC 13) 1,2,4 trimethylbenzene + tert-butylbenzene, 0.097 ppmC 14) decane + secbutylbenzene 15) 1,2,3 trimethylbenzene, 0.019 ppmC 16) dimethylethylbenzene, 0.062 ppmC 17) napthylene, 0.083 ppmC 18) 2-methylnapthylene, 0.0313 ppmC 19) 1-methylnapthylene, 0.015 ppmC.

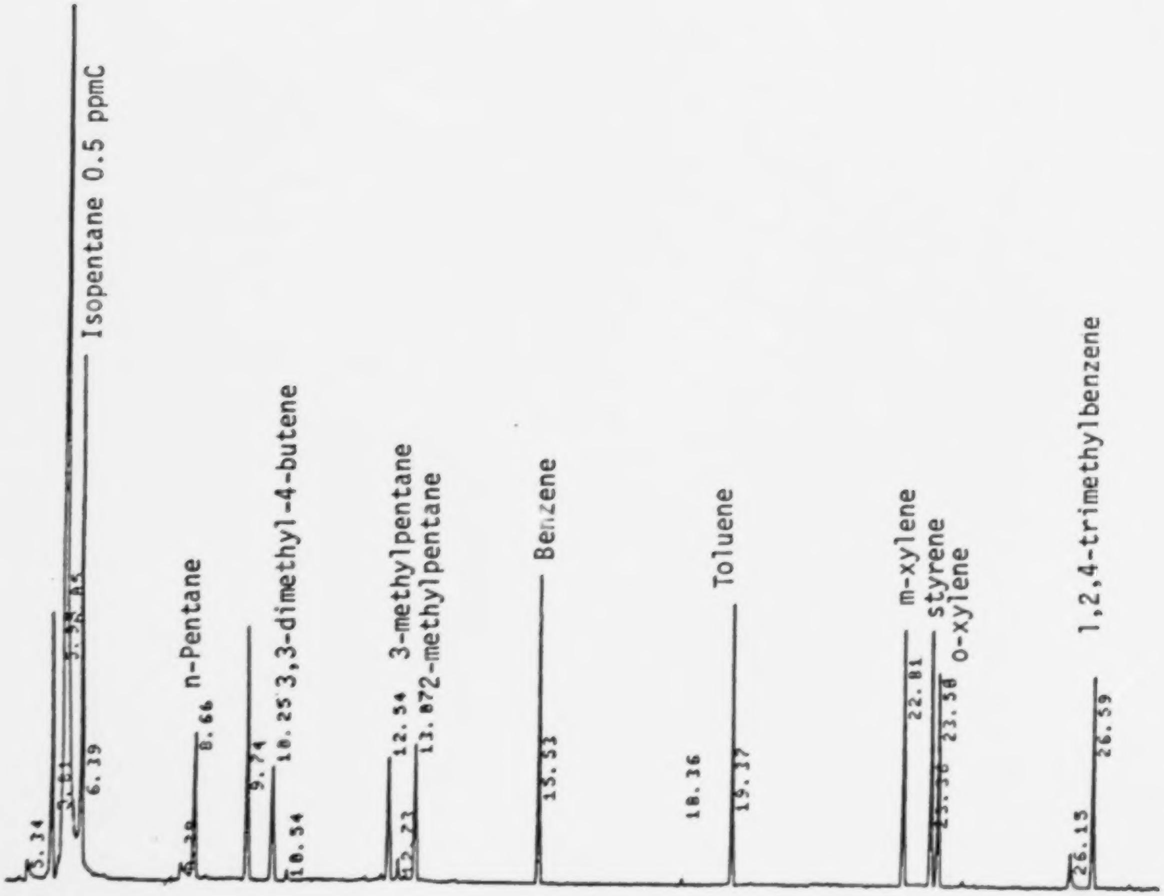


**Figure 11.** Chromatograph of calibration mixture on auto sampling Perkin Elmer Sigma 1 capillary gas chromatograph with 30 m DB-1 column (J&W). 30 cc air sample (with 0.5 ppmC of each alkane and 1 ppmC of each aromatic) to auto $LN_2$ trap, oven = -40°C hold (5 min hold) program rate 5°C/min to 150°C, final hold 5 min. Signal attenuated 10 fold.

meters of the column are coiled into a cup of liquid nitrogen so that on-column trapping of the sample can be accomplished. The oven is then programmed from 10°C to 150°C at 5°C/min. Identification is performed by comparison to the mass spectrum from authentic samples and to literature spectra available in the EPA-NIEHS mass spectra libraries. An analysis of raw auto exhaust and gasoline is shown in the reconstructed ion chromatographs in Figure 12 and Figure 13. Figure 14 is a library mass spectrogram of napthalene and Figure 15 is the mass spectrogram of peak 43 in Figure 12, and there is little doubt that peak 43 is napthalene.

Quantification of individual hydrocarbon species is performed on an "off line" Carlo Erba 4130 FID gas chromatograph. The same fused silica column, cryotrap and temperature program which were used for the GCMS analysis are used here. Identifications are made by comparing the FID chromatogram (Figure 16) with the GCMS reconstructed ion chromatograms. Response factors are determined from a mixture of 15 authentic compounds which are analyzed on the Carlo Erba.

## Formaldehyde by Automated Colorimetry

Since 1979, UNC has used an automated colorimetric formaldehyde instrument manufactured by CEA corporation (Westwood, NJ). This system employs a reverse West and Gaeke technique and hence requires a constant supply of wet chemicals which include highly purified pararosanaline, mercuric chloride, sodium chloride, and sodium sulfite.

Liquid standards are prepared from 37% formalin solution and diluted in the same sodium tetra mecurate (TMC) used in the instrument. A dynamically generated HCHO airstream using a formaldehyde permeation tube (Metronics corporation, Santa Clara, CA) is used to supply known levels of gas phase formaldehyde. In addition, calibration samples of formaldehyde are prepared in the chamber. The chamber is usually dried to a dew point of less than 60°F and known quantities of solid paraformaldehyde are then injected. During the course of a 6 month data season when the chambers are in operation, we have found this system's calibration not to change by more than 10%.

The maximum analytical sensitivity of this instrument is 20 ppb and a continuous sample on each chamber is taken every 30 minutes. Using the solutions recommended by CEA we observed ≈ 5% positive interference from acetaldehyde in the concentration range of 01.-1 ppmV. When appreciable acetaldehyde is generated, the HCHO data are adjusted to subtract out the positive acetaldehyde interference. Interferences from other carbonyls such as acetone, propionaldehyde, MEK or methacrolein produced are not significant. Finally, the system that we

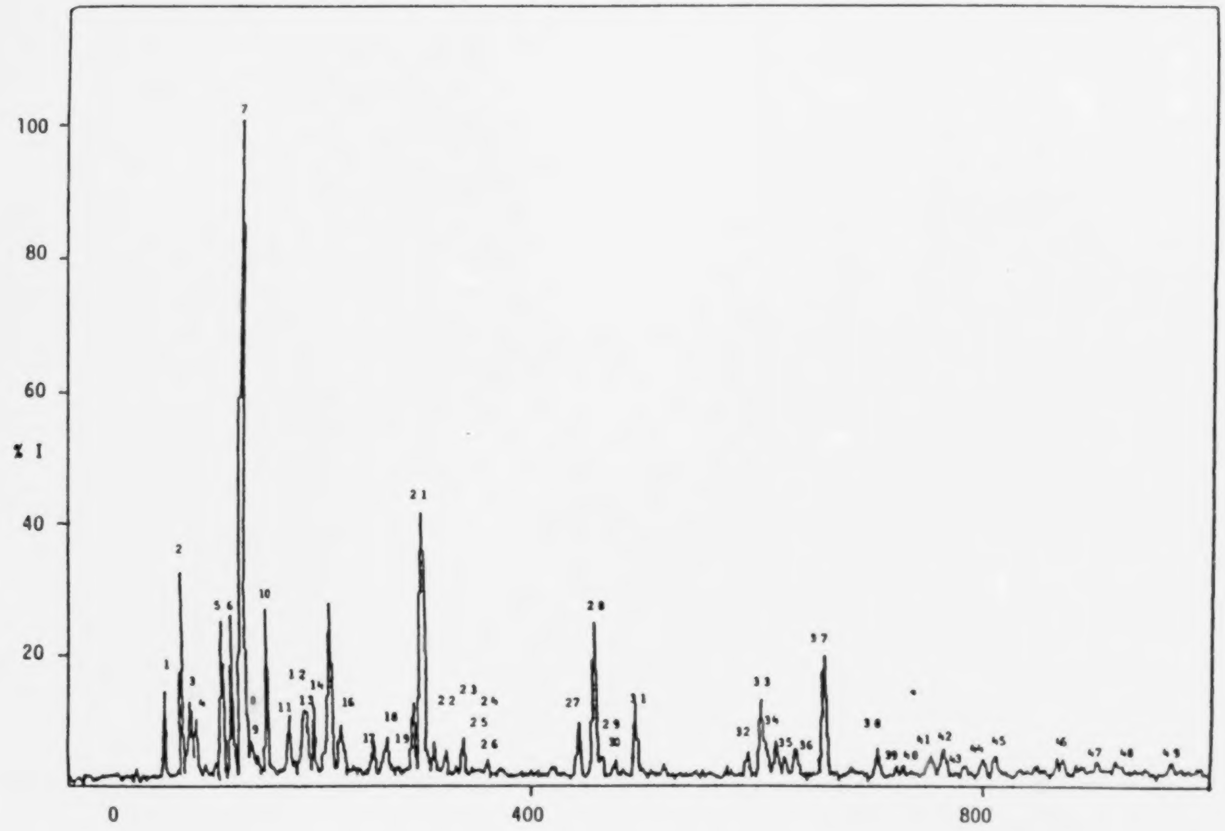


**Figure 12.** Reconstructed ion chromatograph of EPA summer gasoline using DB-1 column. Identities based on comparison with literature mass spectra. Compounds listed in order of elution are: 1) n-butane 2) 2-methylbutane 3) n-pentane 4) methylbutene or 2-pentane 5) 2-methylpentane 6) 3-methylpentane 7) n-hexane 8) hexadiene or a methylcyclopentene + a hexene 9) e-methyl-2-pentene 10) methylcyclopentane 11) benzene 12) 2- methylhexane 13) 2,3-dimethylpentane 14) 3-methylhexane 15) 2, 2,4-trimethylpentane 16) n-heptane 17) methylcyclohexane 18) 2 ,5-dimethylhexane 19) 2,4-dimethylhexane 20) 2,3,4- trimethylpentane or 4-methylheptane 21) toulene 22) 2,3- dimethylhexane 23) 2-methylheptane 24) 3-methylheptane 25) 2,2 ,4- or 2,2,5-trimethylhexane 26) n-octane 27) ethylbenzene 28) m- and/or p-xylenes 29) methylpentanes 30) 3-ethylheptane 31) xylene 32) n-propylbenzene 33) m- and/or p-ethyltolune 34) 1,3 ,5-trimethylbenzene 35) 2- or 4-methylnonane 36) p-ethyltoluene 37) 1,2,4-brimethylbenzene 38) 1,2,3-trimethylbenzene 39) n- decane and other $C_10$ alkylbenzene 40) indan or a methylstyrene 41) sec-butylbenzene and other $C_4$ alkylbenzene (m-tp-n-propyltoluenes and maybe some tert–butylbenzene) 42) n- butylbenzene and other $C_4$ alkylbenzene (maybe some diethylbenzenes) 43) n-propyltoluene and some undecane 44) dimethylethylbenzenes 45) a dimethylethylbenzene 46) tetramethylethylbenzenes 47) $C_5$ alkylbenzene and $C_4$ alkenebenzene 48) $C_4$ alkenebenzene 49) naphthalene.

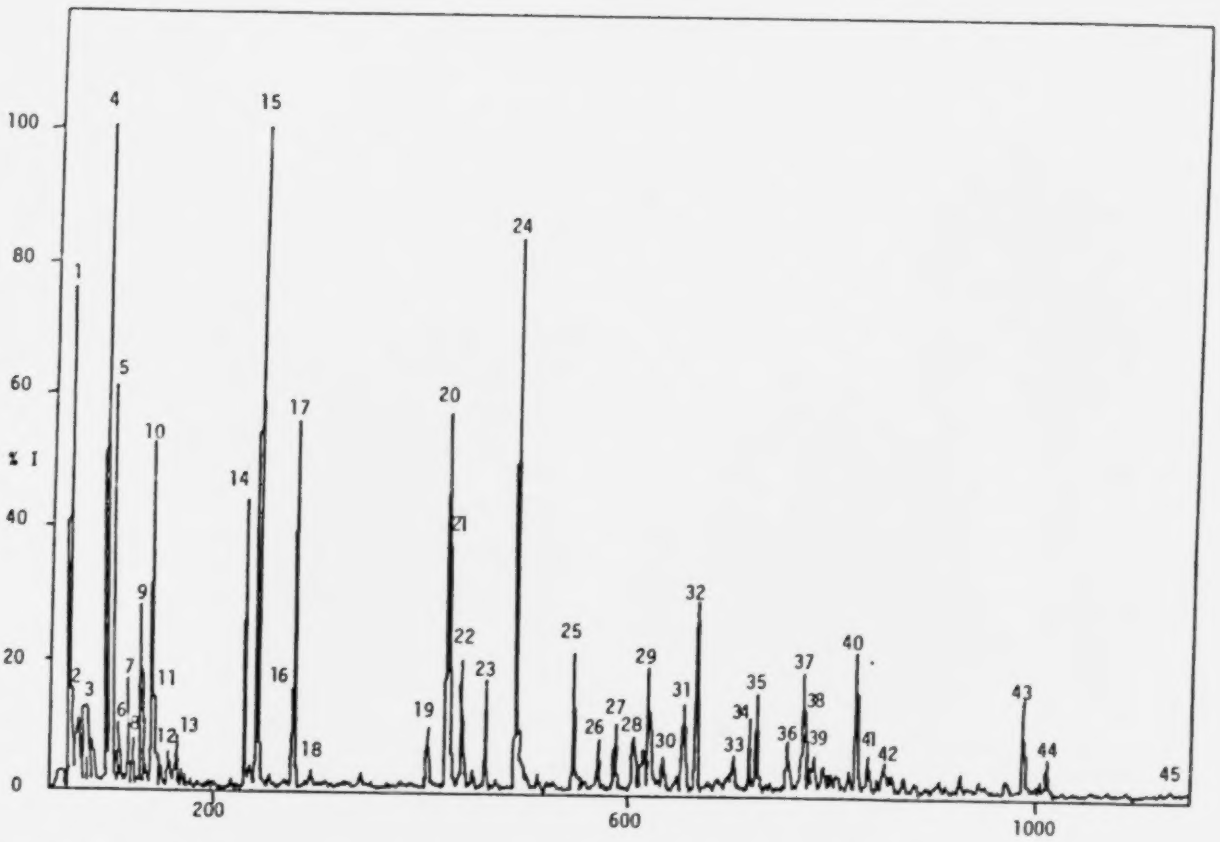


**Figure 13.** Reconstructed ion chromatograph of 1972 Dodge Charger exhaust, running 2200 rpm, using EPA summer gasoline, with 30 m SE54 column. Identities based on comparison with literature mass spectra, compounds listed in order of elution are: 1) butadiene and a butene or cycle-butane 2) 2-methylbutane 3) a pentadiene, or methylbutene; cyclopentadiene, 2-methylpentane, several hexenes; methylcyclopentane 4) benzene 5) 2,2,3 or 2,2,4- trimethylpentane 6) n-heptane + heptene + heptadiene 7) methylcyclohexane 8) 2,4-dimethylhexane 9) a trimethylcyclopentane then 2,3,3-trimethylpentane and 2,3- dimethylhexane 10) toluene 11) 3-methylheptane then 2,2,4- or 2, 2,5-trimethylhexane or 2,2-dimethylheptane 12) 2-ethyl-1-hexane 13) n-octane + trace of an octene 14) ethylbenzene 15) m- and p-xylenes 16) styrene 17) o-xylene 18) isopropylbenzene 19) n -propyl-benzene 20) m-ethyltoluene 21) p-ethyltoluene 22) 1,3, 5-trimethylbenzene 23) o-ethyltoluene 24) 1,2,4- trimethylbenzene and small amount of methylstyrene or indan 25) 1,2,3-trimethylbenzene 26) indan or a methylstyrene 27) indene 28) sec-butylbenzene and some m & p-n,propyl-toluene and maybe some t-butylbenzene; then n-propyltoluene; then n-butylbenzene and some diethylbenzene 29) a dimethylethylbenzene 30) po-n, propyltoluene 31) a dimethylethylbenzene 32) a dimethylethylbenzene and trace $C_4$ alkenebenzene 37) a $C_4$ ene and a $C_6$ alkylbenzene 38) a tetramethylbenzene 39) a $C_6$ alkylbenzene 40) naphthalene 41) a $C_6$ alkenebenzene 42) a pentylbenzene 43) 2-methylnaphthalene 44) 1- methylnaphthalene 45) a dimethyl-naphthalene

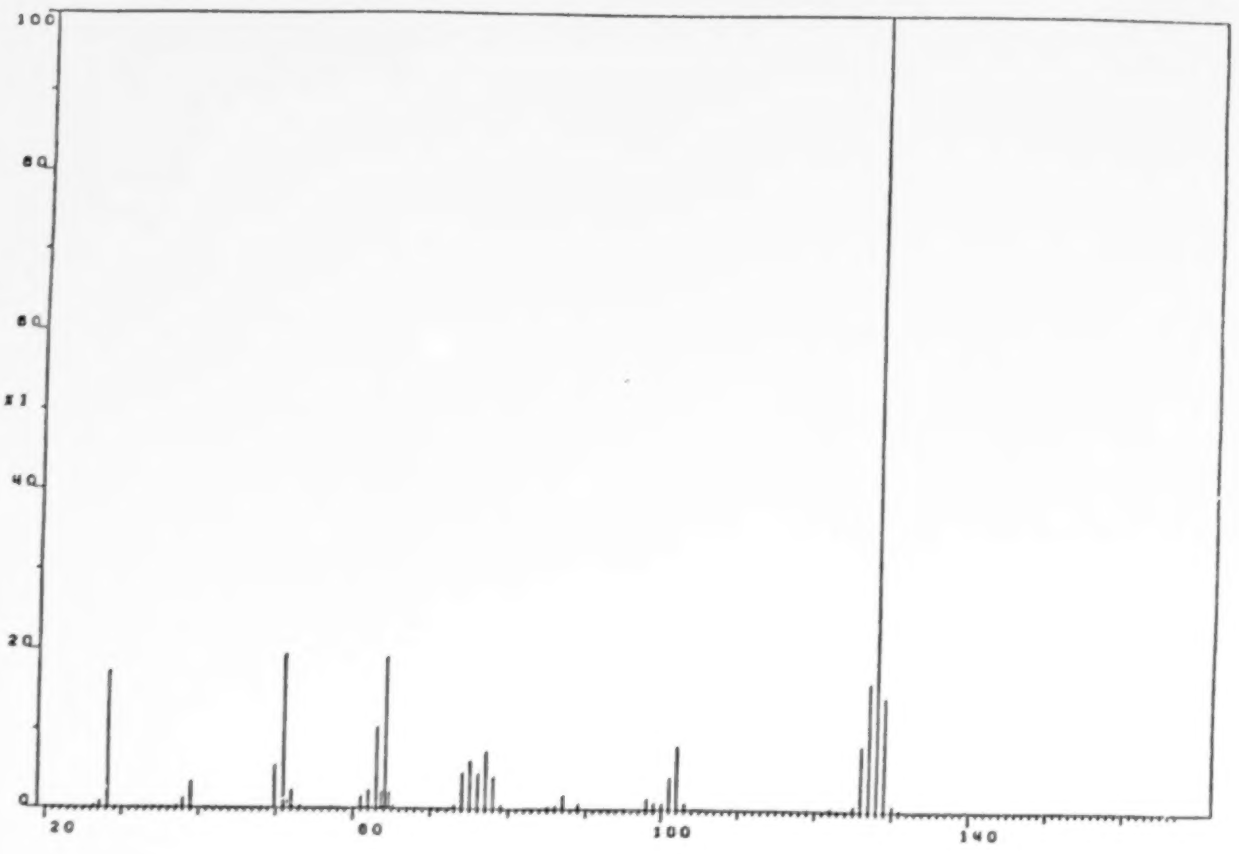


Figure 14. Library mass spectrogram of Naphthalene on the VG Micro-Mass 707F Mass Spectrometer.

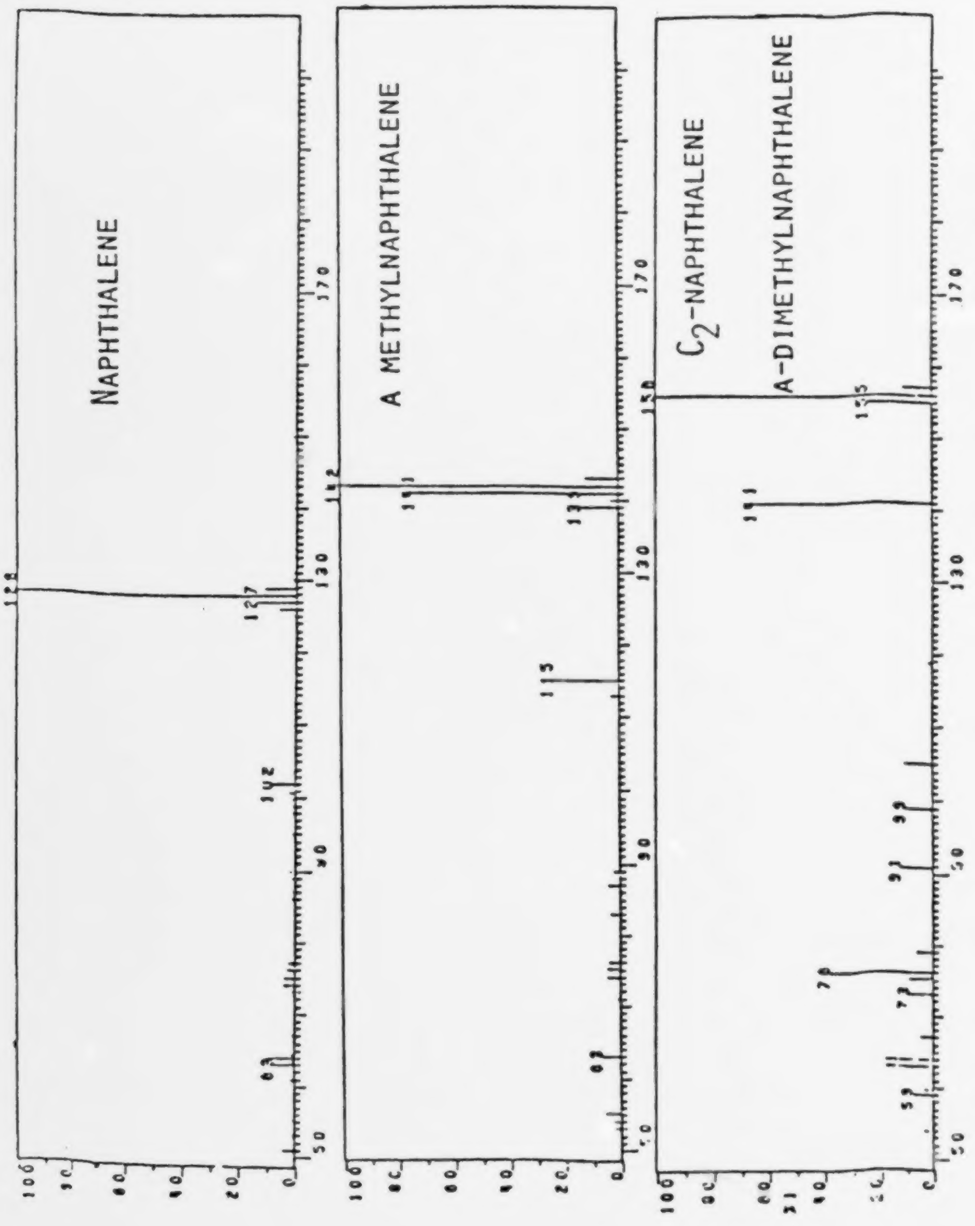


Figure 15. Mass spectrograms of Peaks 43, 44, and 45 of Figure 12, Auto Exhaust.

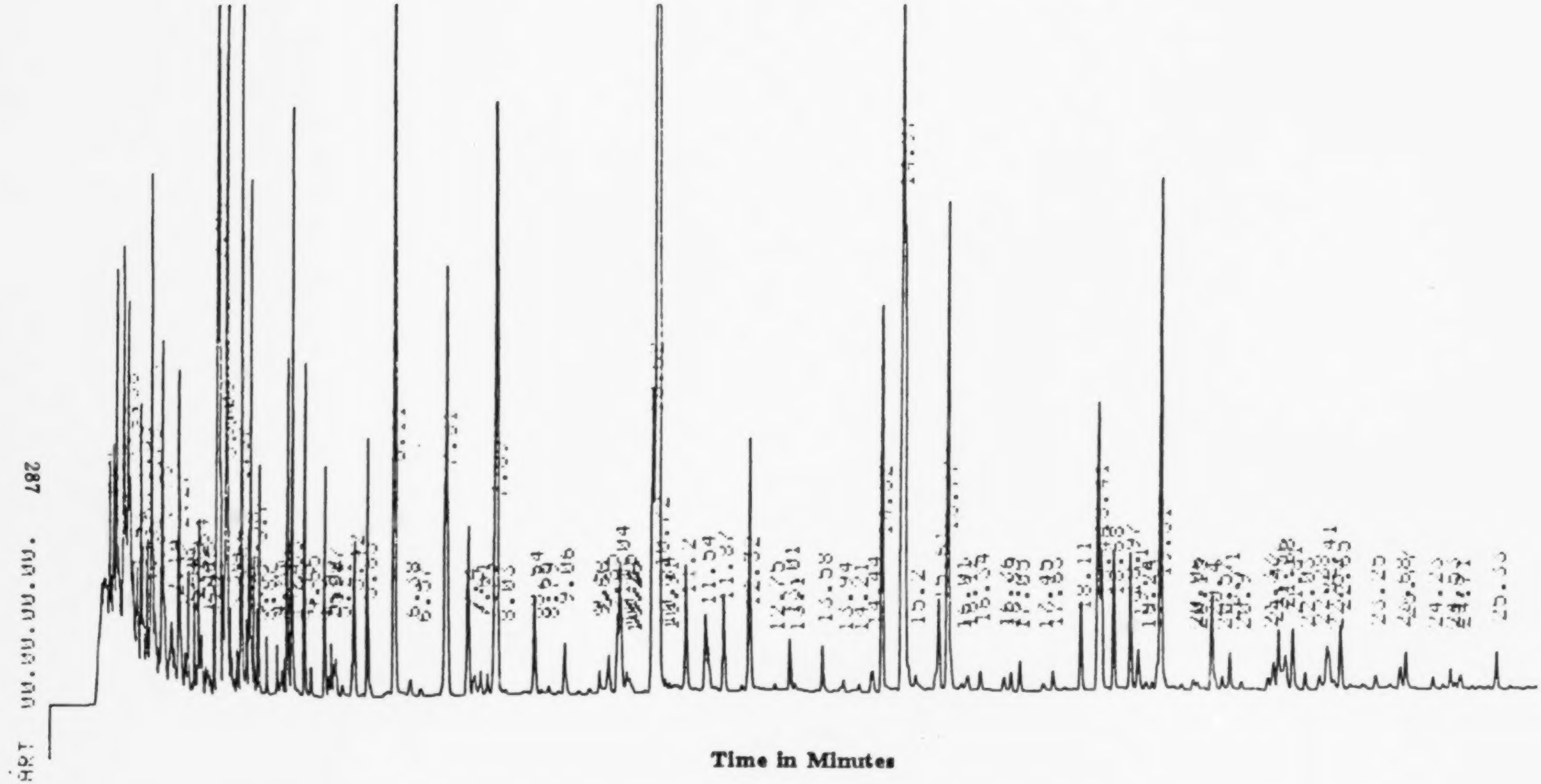


**Figure 16.** Hydrocarbon species identified in cryocondenser auto exhaust (7-28-83) on Carlo Erba-FID gas chromatograph 30 m DB-1 column (J&W) on column liquid oxygen freeze out. Temperature programmed 10°C hold 7 minutes program at 5°C/min to 150°C. Identities bases on comparison with reconstructed ion chromatographs generated under similar operating conditions. 1) 2,3-dimethylbutane 2) 2-methylpentane 3) 3-methylpentane 4) n- hexane 5) methylcyclopentane 6) 2,2- and/or 2,4-dimethylpentane 7) benzene and some methylcyclopentene 8) cyclohexane 9) 2- methylhexane 10) 3-methylhexane 11) 2,2,4-trimethylpentane 12) n-heptane 13) methylcyclohexane 14) 2,4-dimethylhexane 15) toluene 16) 2,3-dimethylhexane 17) n-octane 18) 2,5- dimethylheptane 19) ethylbenzene 20) m-& p-xylene 21) 3- methyloctane 22) o-xylene 23) n-propylbenzane 24) m-& p- ethyltoluene 25) 1,3,5-trimethylbenzene 26) o-ethyltoluene 27) 1,2,4-trimethylbenzene 28) 1,2,3-trimethylbenzene 29) indan 30 ) $C_4$-benzene 31) methylindans 32) naphthalene.

have been using exhibits a 30-50% zero drift over a 3-4 hour period. This drift does not affect the span response but requires frequent zero samples. Examples of the system's response to 1.2 and 0.5 ppmC formaldehyde air samples are shown in Figure 17.

## Carbonyl Analysis

The analysis of $C_1$-$C_8$ carbonyl species in ambient air by reaction with 2,4 dinitrophenylhydrazone (DNPH) and subsequent reverse phase high pressure liquid chromatography of the hydrazone derivatives has been reported by Kuwata *et al.* This procedure is fairly specific and can also be used to measure dicarbonyls.

Ambient aldehydes are sampled with an impinger arrangement into an absorbing reagent which contains acidified DNPH. Three to four recrystallizations of the DNPH with acetonitrile (ACN) are required to remove impurities from the DNPH. The absorbing reagent is prepared by dissolving 0.25 g of purified DNPH in one liter of HPLC grade ACN. This is followed by the addition of 0.2 ml of $H_2SO_4$. Two ml of absorbing reagent are used in a Mae West type bubbler with a sample flow rate of one l/min. This yields a 75% collection for most of the carbonyl compounds which have been tested. These include formaldehyde, acetaldehyde, propionaldehyde, methylvinylketone, benzaldehyde, glyoxal, methylglyoxal, biacetyl and o-tolualdehyde.

Analysis is performed on a Varian 5010 HPLC with a Varian micropak MCH-10 reverse phase, 30 cm, 9 mm column and a fixed 254 nm detector. To eliminate interferences from toluene and xylenes a 365 nm cut off filter is used. The system is run isocratically at a 60:40 ACN:$H_2O$ mixture and a solution flow of 1.6 ml/min. High concentration liquid standards in the gas phase equivalent range of 2-6 ppmV were prepared by direct dilution of 5 $\mu$l of authentic knowns into 100 ml of acetonitrile. Five to twenty $\mu$l of this solution were then added to 2 ml of DNPH absorbing reagent. The final DNPH samples were heated in 2 ml Supelco reaction vials at 70°C for 30 minutes. Comparisons with gas phase and liquid calibration samples are made. A sample chromatogram of a mixture of aldehydes, ketones and dicarbonyls is shown in Figure 18.

## PAN Analysis

PAN measurements are made on a 1/8" × 36" glass column packed with 10% carbowax 600 on Gas chrom G (60-80 mesh) and detected with a Varian 940 electron capture detector. Both the column and the detector are held at room temperature and 5% methane-argon is used as the carrier gas. A 6-port auto sample valve was

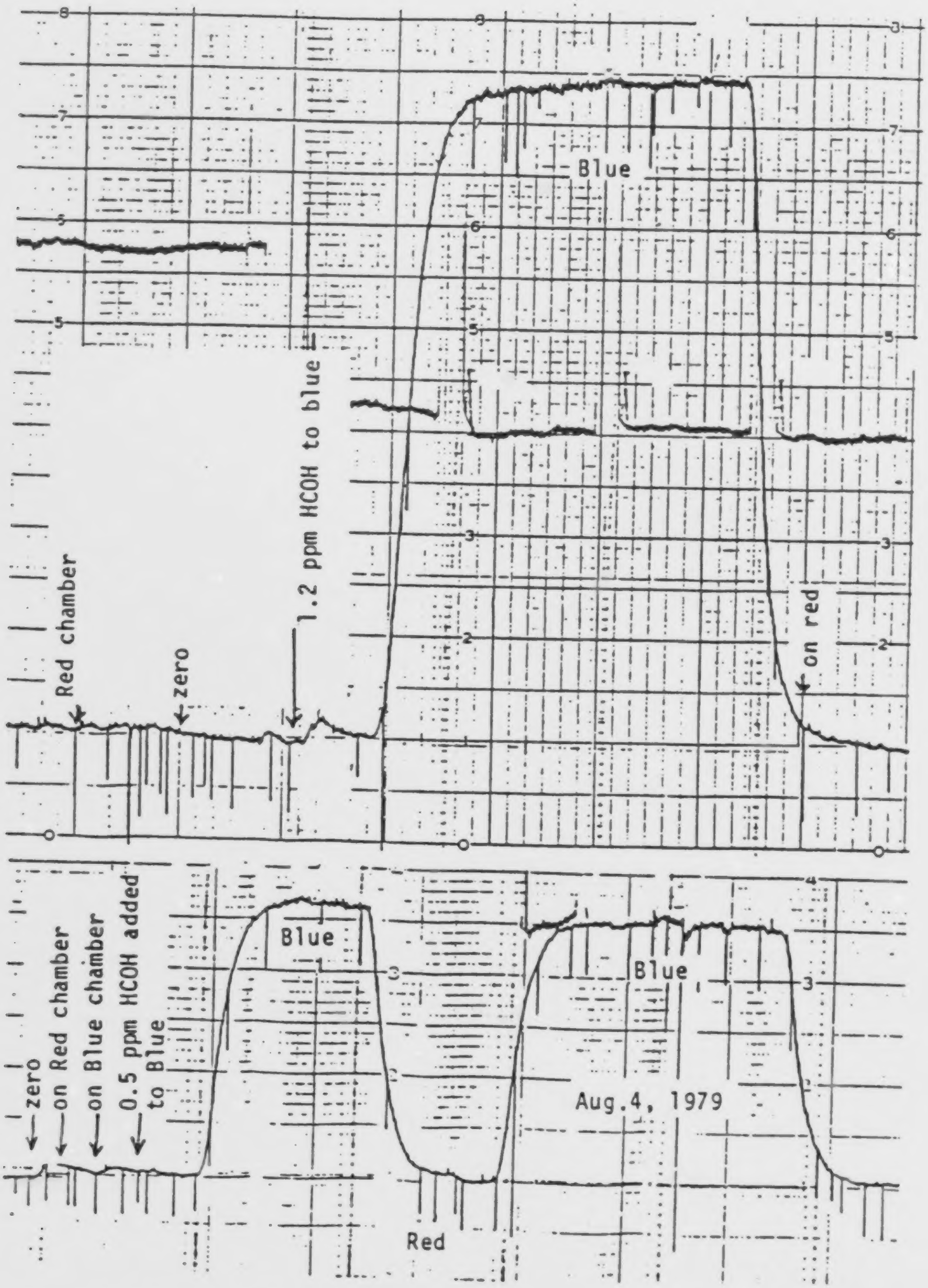


Figure 17. Response of CEA Auto Formaldehyde Instrument to 0.5 and 1.2 ppm of HCOH injected in dry UNC chambers on August 4, 1979 and August 5, 1979.

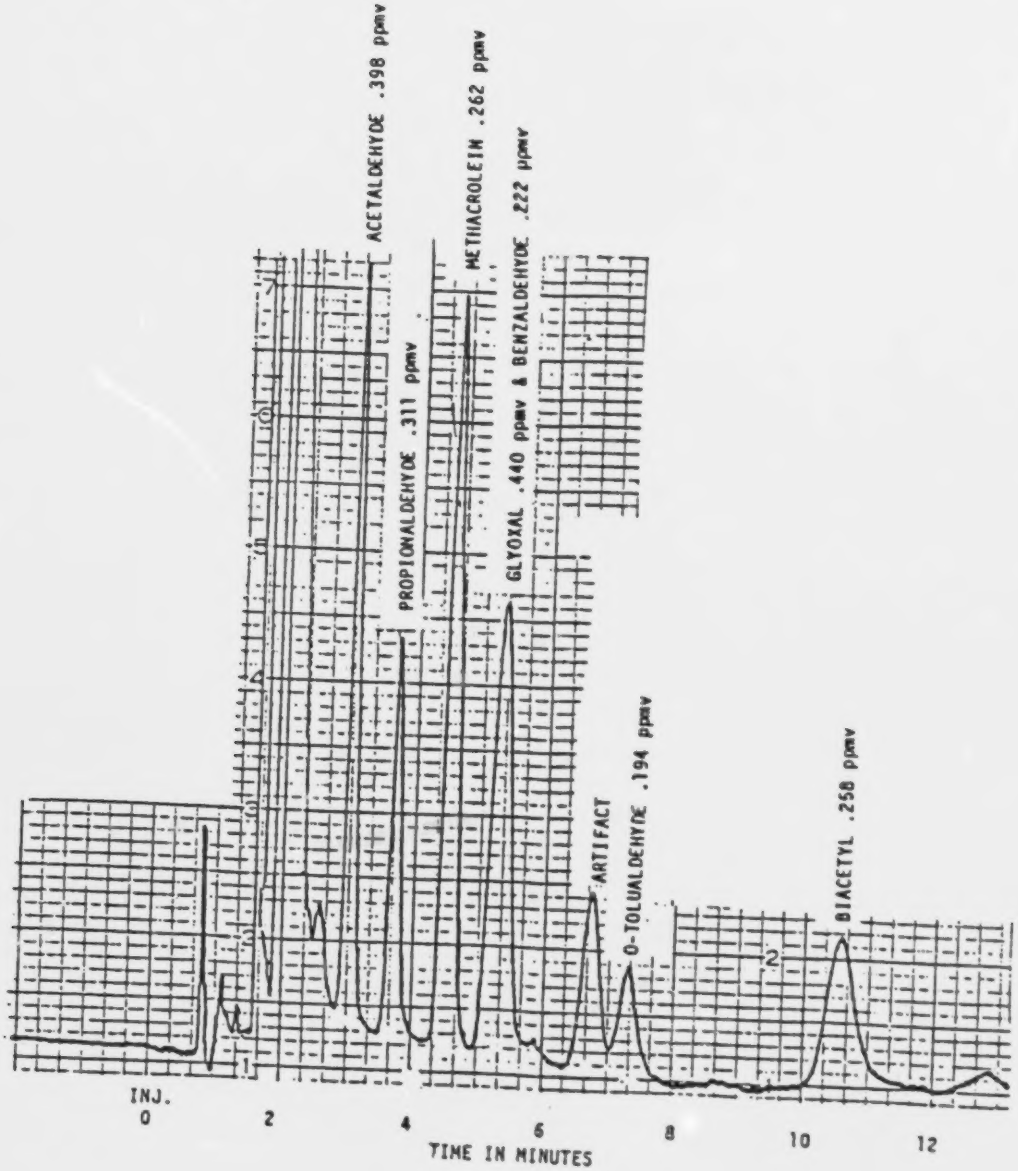


Figure 18. An example of the response of the HPLC with DNPH Method.

installed so that unattended sample injection and analysis can be performed. With a standing current of $20 \times 10^{-9}$ amps we found good response linearly between 0.01 ppmV and 0.5 ppmV of PAN. The response of this system to 0.12 ppmV of PAN is shown in Figure 19.

PAN calibration samples are prepared from an irradiated biacetyl-$NO_2$ bag system. The PAN is purified with a 10% Carbowax 600 prep-column (25 cm × 7 mm) and a liquid nitrogen freeze-out concentrator. PAN from the cryotrap is then diluted into a clean Teflon bag and measured with a calibrated chemiluminescence $NO_x$ analyzer. The response of the chemiluminescent monitor to PAN is 100% and thus pure PAN sample can be standardized. When this procedure is not possible 4 ppmC and 0.5 ppm of propylene $NO_x$ (40% $NO_2$) are irradiated outdoors for 3-4 hours during the mid-morning and the early afternoon. With a chemiluminescent $NO_x$ meter, the $NO_2$ concentrations are followed beyond the $NO_2$ peak until $NO_2$ stabilizes. The PAN GC responses are then keyed to chemiluminescent PAN readings.

## Alkynitrates

The $C_1$-$C_6$ alkylnitrates can be detected on the same system that is used to measure PAN. Calibration for ethyl, isopropyl, propyl, and butylnitrates were performed by injecting microliter volumes of the authentic samples into the outdoor chambers and applying the appropriate dilution and temperature factors (Figure 20). Calibration factors for compounds for which we did not have authentic samples (*e.g.* sec-butylnitrate and isopentylnitrate) were estimated from the ECD response of n-butylnitrate. An uncertainty of +40% is then assigned to these latter compounds.

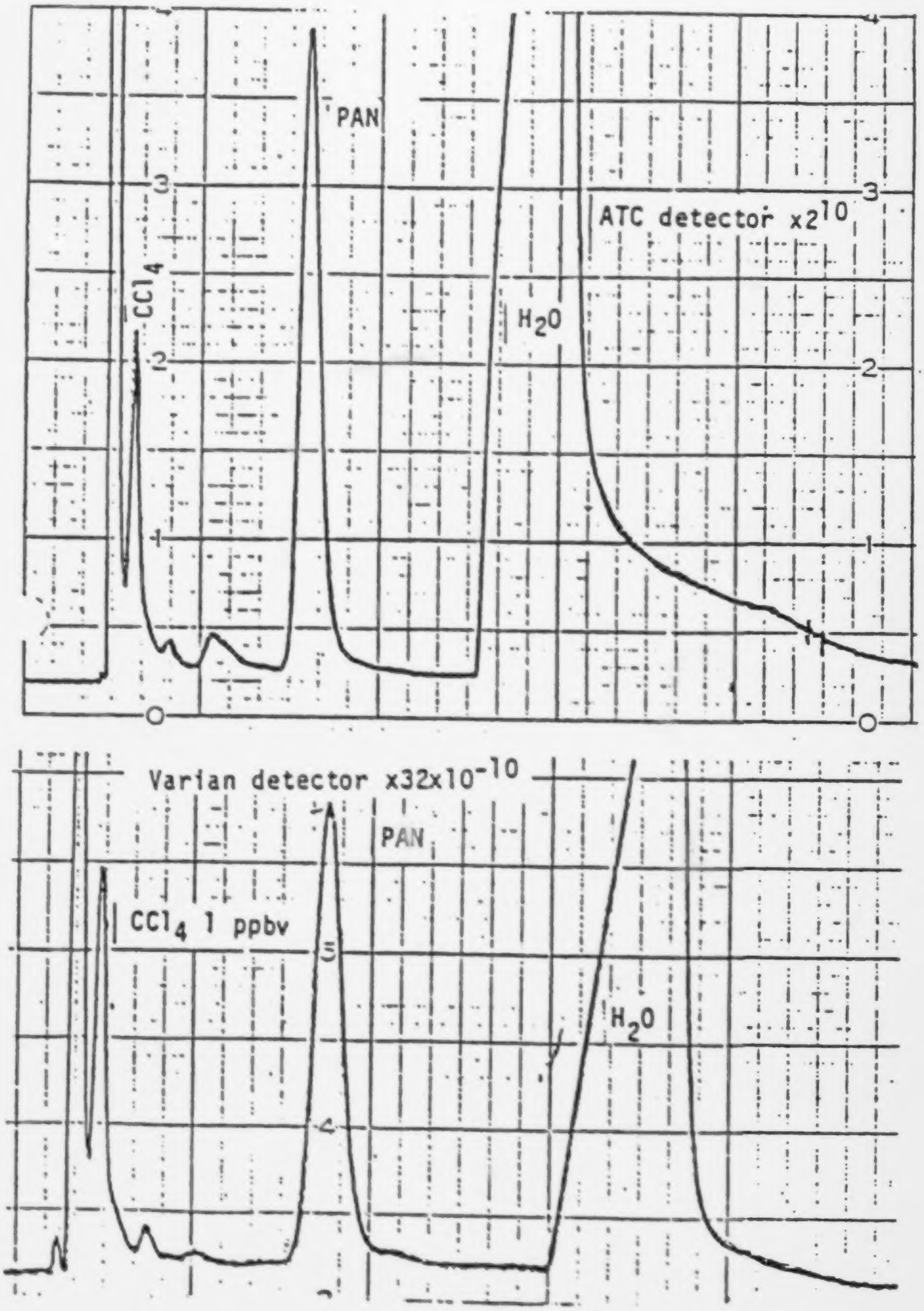


Figure 19. Response of two UNC electron capture detectors to 0.12 ppmV PAN May 1978.

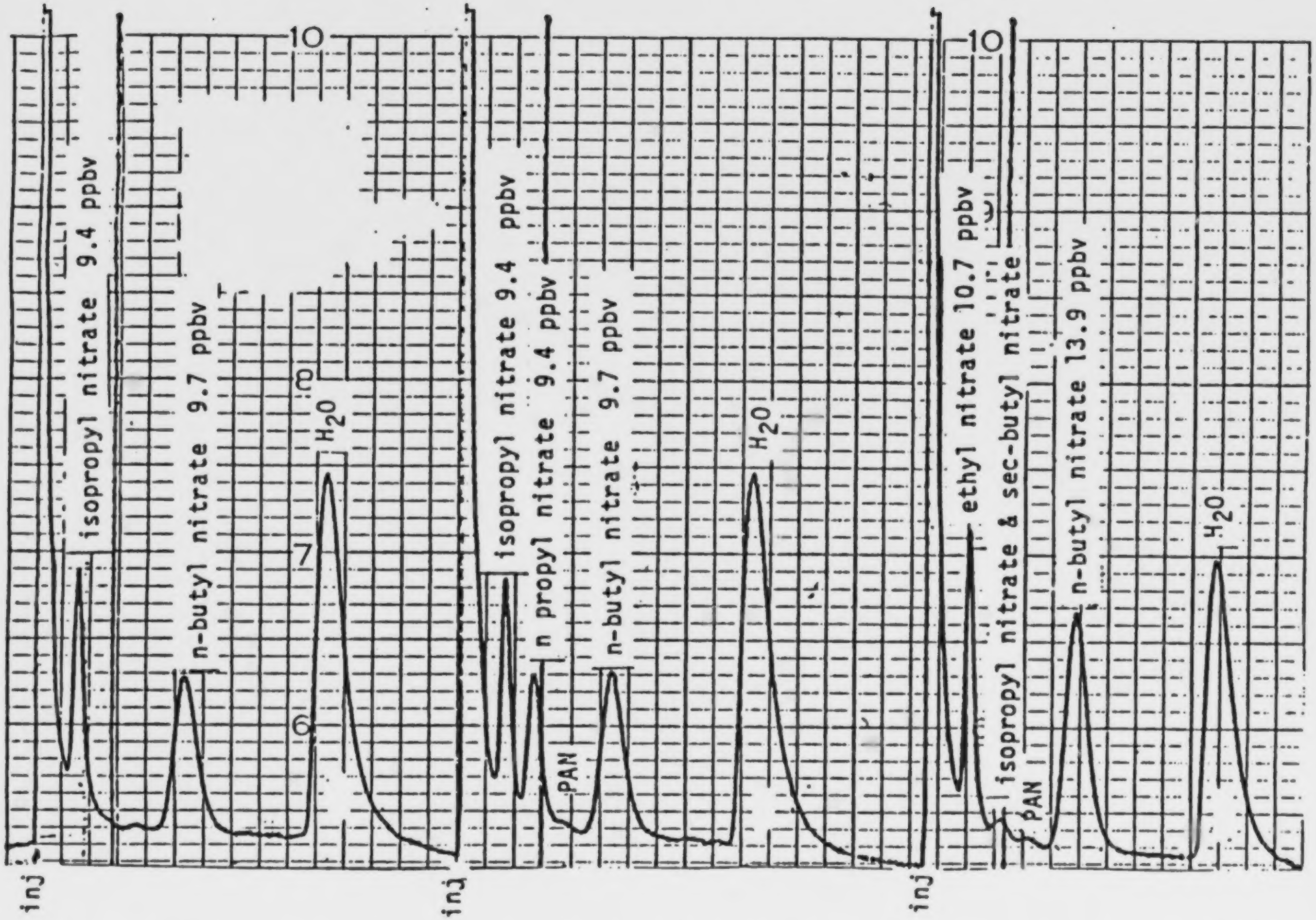


**Figure 20**. Detection of alkylnitrates with automated PAN GC, Varian 940 ECD. $N_2$ flow = 5 cc/min, oven and detector at 24.5°C, standing current on $32x10^{-9}$ amps = 91% of full scale, chart = .1"/min, atten. = $x32x10^{-10}$ amps.